33

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Indiana Academy of Science

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April, 1934

PROCEEDINGS

OF THE

Indiana Academy of Science

FOUNDED DECEMBER 29, 1885

VOLUME 43

STANLEY A. CAIN, Editor

Field meeting held at
Clifty Falls State Park and vicinity,
May 25-27, 1933.

Program meeting held at Indiana University,
Bloomington, Indiana
October 12-14, 1933.

TABLE OF CONTENTS

Page

Officers and Committees for 1933 7

Minutes of the Spring Meeting 12

Minutes of the Winter Meeting 13

Memorials—

Ernest Danglade 19

Gerard Fowke (Charles Mitchell Smith) 20

Edward Bruce Williamson 23

Presidential Address, Origins of Indiana's Mammals: Marcus Ward Lyon, Jr. 27

Paper from the General Program—

Indirect Contributions to the Promotion of Science: W. M. Blanchard 44

Papers from the Program of the Botany and Bacteriology Section—

Plants New or Rare to Indiana, XIX: Chas. C. Deam 48

Notes on Indiana Grasses, 1933: J. E. Potzger 50

On Merthiolate and Fungi Associated with Ringworm: H. M. Powell and W. A. Jamieson 56

Insect Galls on Species of Cuscuta: T. G. Yuncker 70

Papers from the Program of the Chemistry Section—

Organic Compounds of Selenium, VI: W. E. Bradt 72

The Adsorptive Capacity of Silicas for Benzene Vapor: K. E. Conn with R. J. Hartman 99

Catalytic Oxidation of the Carbohydrates and Related Compounds by Oxygen in the Presence of Iron Pyrophosphates, III. Ethyl Alcohol, Acetaldehyde, Acetic Acid, and Sodium Acetate: Ed. F. Degering 105

Concerning the Use of Nitro Compounds as Oxidizing Agents: W. A. Fletcher with R. E. Lyons 107

Determination of the Degree of Hydration of Magnesia in Dolomitic Limes: E. L. Fox and F. C. Mathers 113

The Preparation of Hydrogen Selenide by the Interaction of Selenium and Hydrocarbons: Clarence Green and W. E. Bradt 116

Analysis of Group III: Ralph W. Hufferd 118

On the Progenitors of Certain Plant Alkaloids and the Mechanism of their Formation in the Plant Structure: Percy L. Julian 122

Separation of Iron from Indium with Cupferon: F. C. Mathers and C. E. Prichard 125

The Secondary Reactions in the Preparation of Zinc Ethyl: R. F. McCleary and Ed. F. Degering 127

Page

Color Reactions of Amino Acids with Phenols and Hypochlorites, Including New Tests for Tryptophane and Phenylalanine: F. M. Miller and R. E. Lyons 132
A Method for an Oxidizing Hydrolysis of Ozonides Prepared from Unsaturated Acids: J. L. Riebsomer and R. C. Tallman 136
Some Experiments in Coloring Cellophane: L. A. Test 139
The Dissociation Constants of Mono- and Trichloroacetic Acids in Ethyl Alcohol: F. J. Welcher and H. T. Briscoe 142

Papers from the Program of the Geology Section—
The Garrett Mastodon: Paul F. Simpson 154
Some Unusual Geode Forms: W. P. Von Osinski 155

Papers from the Program of the Physics Section—
Multiple Resonance in Violins: R. B. Abbott and R. O. Jenkins .. 158
A New Focusing Device for Electron Diffraction: W. I. Caldwell 159
Magnetic Effect on a Vibrating Quartz Crystal Excited Piezo-Electrically: S. H. Cortez 161
Effect of Sound on Space Currents: S. E. Elliott 163
Methods of Measuring Surface Potentials: J. E. Ferguson 169
Radio Field Intensity Measurements about Athens, Ohio: D. B. Green and R. V. Kelch 171
The Effect of Position upon the Efficiency of Acoustical Treatment: D. L. Harmon 175
An X-Ray Investigation of Orientated Dielectrics: K. Lark-Horovitz and A. N. Ogden 182
The Hall and Allied Effects in Cast Bismuth Plates as Affected by the Rate of Cooling: L. H. Petersen 185
Character of the ^3S Terms in the Mercury Spectrum: I. Walterstein 190

Physics Teaching Notes—
The Production of Liquid Oxygen as a Lecture Table Demonstration: Chas. T. Knipp 192
A New Lecture Table Demonstration to Show that Cathode Rays Leave the Cathode Normally: Chas. T. Knipp 192
A Rotator Accessory for Showing by Analogy the Apparent Deflection of a Projectile Due to the Rotation of the Earth on Its Axis: R. V. Cook 193
The Formation of Nodes and Loops on a Weighted Cord by Means of a Rotator: R. V. Cook 194

Papers from the Program of the Zoology Section—
Insects of Indiana for 1933: J. J. Davis 195
The Effect of Lowered Temperature on Reticulocyte Formation in the Pigeon: D. G. Graam 201
Certain Factors Influencing the Respiratory Metabolism of the Leech (*Hirudo medicinalis*): Wm. A. Hiestand and J. I. Singer 205

Page

Records of Indiana Dragonflies—VII. 1932-33: B. E. Montgomery 211
Macrobrachium Ohionis, The Large Fresh-Water Shrimp: R. N. McCormick 218
The Effect of Ultraviolet Irradiation upon Fecundity of *Drosophila melanogaster:* E. B. Steen..... 224
Birds of Tippecanoe County IV: L. A. Test and F. H. Test.... 228
The Gross Anatomy of a Two-Bodied Lamb: T. W. Torrey.... 235

Membership List 238

Junior Academy of Science Chapters..... 262

Index 263

OFFICERS AND COMMITTEES FOR 1933

President, Marcus W. Lyon, Jr., South Bend.
Vice-President, M. S. Markle, Earlham College.
Secretary, Ray C. Friesner, Butler University.
Assistant Secretary, W. P. Morgan, Indiana Central College.
Treasurer, Paul Weatherwax, Indiana University.
Press Secretary, W. E. Edington, DePauw University.
Editor, Stanley A. Cain, Indiana University.
Trustees, Academy Foundation, Frank B. Wade (Term expires 1935), Shortridge High School, Indianapolis; John S. Wright (Term expires 1936), Eli Lilly Company, Indianapolis.
Committee for Bonding Trustees, H. L. Bruner, Butler University; W. A. Cogshall, Indiana University. (This committee is appointed by the Executive Committee.)

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(Officers and Past Presidents)

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Behrens, C. E.
Blanchard, W. M.
Blatchley, W. S.
Bruner, H. L.
Burrage, S.
Butler, A. W.
Cain, S. A.
Cogshall, W. A.
Coulter, Stanley
Cumings, E. R.
Davis, J. J.
Deam, C. C.
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Edington, W. E.
Fisher, M. L.
Friesner, R. C.
Hessler, R.
Lyon, Jr., M. W.
Mahin, E. G.
Morgan, W. P.
Moenkhaus, W. J.
Mottier, D. M.
Naylor, J. P.
Nieuwland, J. A.
Noyes, W. A.
Payne, F.
Ramsey, R. R.
Rettger, L. J.
Wade, F. B.
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Wright, J. S.

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R. B. ABBOTT, Purdue University
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H. L. BRUNER, Butler University
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Nominations

To be announced later.

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FRANK B. WADE, Indianapolis
O. B. CHRISTY, Ball Teachers College
L. J. RETTGER, Indiana State Teachers College
O. C. OSBORNE, South Bend High School

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S. A. CAIN, Indiana University
E. G. MAHIN, University of Notre Dame
JOHN S. WRIGHT, Indianapolis
J. J. DAVIS, Purdue University
W. N. COGSHALL, Indiana University

PAST OFFICERS OF THE INDIANA ACADEMY OF SCIENCE

YEAR	PRESIDENT	SECRETARY	PRESS SECRETARY	TREASURER	‡EDITOR
1886[1]	*David S. Jordan	Amos W. Butler		O. P. Jenkins	
1887	*John M. Coulter	Amos W. Butler		O. P. Jenkins	
1888	*J. P. D. John	Amos W. Butler		O. P. Jenkins	
1889	*John C. Branner	Amos W. Butler		O. P. Jenkins	
1890	*T. C. Mendenhall	Amos W. Butler		O. P. Jenkins	
1891	*O. P. Hay	Amos W. Butler		O. P. Jenkins	
1892	*J. L. Campbell	Amos W. Butler		C. A. Waldo	
1893	J. C. Arthur	Amos W. Butler		C. A. Waldo	
1894	W. A. Noyes	C. A. Waldo		W. P. Shannon	
1895	Amos W. Butler	John S. Wright		W. P. Shannon	C. A. Waldo
1896	Stanley Coulter	John S. Wright		W. P. Shannon	C. A. Waldo
1897	*Thomas Gray	John S. Wright		W. P. Shannon	C. A. Waldo
1898	*C. A. Waldo	John S. Wright	Geo. W. Benton	J. T. Scovell	G. W. Benton
1899	*C. H. Eigenmann	John S. Wright	Geo. W. Benton	J. T. Scovell	G. W. Benton
1900	*D. W. Dennis	John S. Wright	Geo. W. Benton	J. T. Scovell	G. W. Benton
1901	*M. B. Thomas	John S. Wright	Geo. W. Benton	J. T. Scovell	D. Bodine
1902	*Harvey W. Wiley	John S. Wright	Geo. W. Benton	J. T. Scovell	D. Bodine
1903	W. S. Blatchley	John S. Wright	G. A. Abbott	W. A. McBeth	W. J. Karsla
1904	*C. L. Mees	John S. Wright	G. A. Abbott	W. A. McBeth	D. Bodine
1905	John S. Wright	B. McMullen	G. A. Abbott	W. A. McBeth	E. G. Martin
1906	Robert Hessler	B. McMullen	Charles R. Clark	W. A. McBeth	A. L. Foley
1907	D. M. Mottier	B. McMullen	G. A. Abbott	W. A. McBeth	L. B. McMullen
1908	*Glenn Culbertson	J. H. Ransom	G. A. Abbott	W. A. McBeth	H. L. Bruner
1909	A. L. Foley	J. H. Ransom	G. A. Abbott	W. A. McBeth	H. L. Bruner
1910	*P. N. Evans	Geo. W. Benton	J. W. Woodhams	W. J. Moenkhaus	L. J. Rettger
1911	*C. R. Dryer	A. J. Bigney	Milo H. Stuart	W. J. Moenkhaus	L. J. Rettger
1912	J. P. Naylor	A. J. Bigney	Milo H. Stuart	W. J. Moenkhaus	C. C. Deam

PAST OFFICERS OF THE INDIANA ACADEMY OF SCIENCE—Continued

Year	President	Secretary	Press Secretary	Treasurer	‡Editor
1913	*Donaldson Bodine	A. J. Bigney	F. B. Wade	W. J. Moenkhaus	H. E. Barnard
1914	Severanee Burrage	A. J. Bigney	F. B. Wade	W. A. Cogshall	H. E. Barnard
1915	W. A. Cogshall	A. J. Bigney	F. B. Wade	Wm. M. Blanchard	H. E. Barnard
1916	*A. J. Bigney	H. E. Enders	F. B. Wade	Wm. M. Blanchard	L. F. Bennett
1917	W. J. Moenkhaus	H. E. Enders	F. B. Wade	Wm. M. Blanchard	L. F. Bennett
1918	E. B. Williamson	H. E. Enders	F. B. Wade	Wm. M. Blanchard	L. F. Bennett
†1919	E. B. Williamson	H. E. Enders	F. B. Wade	Wm. M. Blanchard	F. Payne
1920	H. L. Bruner	H. E. Enders	F. B. Wade	Wm. M. Blanchard	F. J. Breeze
1921	Howard E. Enders	Walter N. Hess	F. B. Wade	Wm. M. Blanchard	F. Payne
1922	F. M. Andrews	Walter N. Hess	F. B. Wade	Wm. M. Blanchard	J. J. Davis
1923	Charles A. Behrens	Walter N. Hess	H. F. Dietz	Wm. M. Blanchard	J. J. Davis
1924	C. C. Deam	Flora Anderson	H. F. Dietz	Wm. M. Blanchard	J. J. Davis
1925	E. R. Cumings	Flora Anderson	H. F. Dietz	Wm. M. Blanchard	J. J. Davis
1926	Wm. M. Blanchard	R. C. Friesner	H. F. Dietz	C. M. Smith	J. J. Davis
1927	Frank B. Wade	R. C. Friesner	H. F. Dietz	M. W. Lyon, Jr.	J. J. Davis
1928	E. G. Mahin	R. C. Friesner	H. F. Dietz	M. W. Lyon, Jr.	J. J. Davis
1929	Louis J. Rettger	R. C. Friesner	H. F. Dietz	M. W. Lyon, Jr.	S. A. Cain
1930	Rolla R. Ramsey	R. C. Friesner	W. E. Edington	M. W. Lyon, Jr.	S. A. Cain
1931	J. J. Davis	R. C. Friesner	W. E. Edington	M. W. Lyon, Jr.	S. A. Cain
1932	F. Payne	R. C. Friesner	W. E. Edington	M. W. Lyon, Jr.	S. A. Cain
1933	Marcus W. Lyon, Jr.	R. C. Friesner	W. E. Edington	Paul Weatherwax	S. A. Cain
1934	J. A. Nieuwland	R. C. Friesner	W. E. Edington	Paul Weatherwax	S. A. Cain

*Deceased. †Officers continued—Annual meeting not held because of influenza epidemic. ‡Listed in year of Proceedings edited.
[The first meeting of the Academy was held Dec. 29, 1885. D. S. Jordan was President for 1885 also.

MINUTES OF THE SPRING MEETING

CLIFTY FALLS STATE PARK

The Indiana Academy of Science met for its regular spring meeting at Clifty Falls State Park, May 25-27, 1933. The meeting was called to order by President Lyon at Clifty Inn. Chairman Cain made a report of proposed changes in the Constitution. These were discussed at length and referred to the winter meetings of the Academy for final action.

Dr. Cain reported the need of $150.00 to clear up all back publication debts. This amount was made necessary because of failure of authors to pay for reprints. On motion properly seconded and passed this amount was made available to the Editor together with the appreciation of the Academy for the good work done.

Dr. Foley reported the names of six applicants for membership. These were unanimously elected. Mr. Esten reported on the progress of the Junior Academy.

At the close of the business session the members present enjoyed a very interesting and instructive address on "Items of Historic Interest" by Mr. Curtis Marshall, President of the Jefferson County Historical Society.

Friday was spent in field trips to the Fourteen-mile Creek area, Rose Island, near Charlestown and to the State Forest near Henryville.

Lunch was served at noon to 50 members by the ladies of the Christian Church of Charlestown, and dinner was served in the evening by the ladies of the Presbyterian Church at Henryville. The Academy members adopted the following resolution, copies of which were sent to the persons concerned.

"The Indiana Academy of Science wishes to take this opportunity to express its gratitude to the many persons who have helped to make its spring meeting a success. We would mention particularly the Management of Clifty Inn and Mr. Curtis Marshall of Madison; the ladies of the Christian Church at Charlestown; the ladies of the Presbyterian Church at Henryville; and Dr. Will Scott, Chairman of the Program Committee.

W. B. ADAMS,
CLYDE MALOTT,
PAUL WEATHERWAX,
Resolutions Committee."

WINTER MEETING

PROGRAM OF THE FORTY-NINTH ANNUAL MEETING
HELD AT
INDIANA UNIVERSITY
October 12-14, 1933

THURSDAY, OCTOBER 12, 1933

3:00 p. m. Meeting of Taxonomists, Biology Hall, Room 26.
6:00 p. m. Executive Committee Dinner, Grill Room, Union Building.
7:00 p. m. Executive Committee, Business Session, Union Building.

FRIDAY, OCTOBER 13, 1933

9:30 a. m. General Session, Alumni Hall, Union Building.
12:00 m. Luncheon, University Cafeteria.
1:30 p. m. Sectional Meetings for all Sections.
4:00 p. m. Entomologists Meeting, Biology Hall, Room 36.
6:00 p. m. Annual Dinner, Alumni Hall, Union Building.
8:00 p. m. President's Address. Origins of Indiana Mammals Living and Extinct. President Marcus W. Lyon, Jr.

SATURDAY, OCTOBER 14, 1933

9:00 a. m. Trip to Stone Mills.
9:00 a. m. Drive through Brown County.
9:00 a. m. Junior Academy of Science, H. E. Enders, Chairman.

MEETINGS OF SECTIONS

Botany and Bacteriology (23 papers). T. G. Yunker, Chairman.
Chemistry (19 papers). Ned Guthrie, Chairman.
Geology and Geography (11 papers). E. R. Smith, Chairman.
Physics and Astronomy (29 papers). K. Lark-Horovitz, Chairman.
Zoology (19 papers). B. H. Grave, Chairman.

MINUTES OF EXECUTIVE COMMITTEE

The Executive Committee was called to order by President Lyon at 7:15 p. m. The following committee members in addition to 32 other Academy members were present: F. M. Andrews, C. E. Behrens, W. M. Blanchard, W. S. Blatchley, W. A. Cogshall, E. R. Cumings, J. J. Davis, C. C. Deam, H. E. Enders, W. E. Edington, R. C. Friesner, M. W. Lyon, Jr., E. G. Mahin, D. M. Mottier, F. Payne, R. R. Ramsey, F. B. Wade and P. Weatherwax. Reports of officers followed:

Academy Foundation. F. B. Wade presented a detailed report of the condition of Foundation funds:

December 1, 1932, balance from previous year	$169.92
Total receipts, including interest and other additions	268.87
Total	$438.79
Investments made including cost of same	427.43
Balance in Indiana National Bank savings account	$11.36

ASSETS

U. S. 4th L. L. Bond	$50.00
U. S. Treasury Bonds	4,100.00
Muncie Masonic Temple, Preferred	200.00
Standard Oil Company of Indiana, Common	150.00
Balance as shown above	11.36
Total par value of assets	$4,511.36

Archaeological Survey. Chairman Guernsey reported intensive studies of aboriginal village sites, earthworks, fortifications, etc., in the region along the Ohio river contiguous to the Ohio Falls in Clark County. As a result of these researches an archaeologic map of Indiana has been published by the Conservation Commission.

Biological Survey. Chairman Montgomery reported that the work of preparing a bibliography of Indiana biota is well under way. The work on Arthropoda is complete except for two orders of Insecta; that of Mammalia, Reptilia and Amphibia is complete; that of Aves is three-fourths done; that of Pisces, partly done. The work on Algae, Bryophyta, Pteridophyta and Spermatophyta is complete but nothing has been done on Fungi. The following recommendations were approved by the Academy: That the Academy do all in its power to insure publication of manuscripts dealing with Indiana fauna and flora; that the Academy encourage younger students in research and in scientific writing; that the state universities be urged to provide adequate facilities for the organization and permanent preservation of specimens of Indiana fauna and flora.

Editor. A lengthy report dealing with the problems of editorial work was made. After much discussion, a committee which should include at least two former editors was authorized to prepare a code of editorial policy and submit it to the Academy at its Spring Meeting. (J. J. Davis, F. Payne, and Theodor Just were appointed on this committee.) In the meantime the Editor was authorized to prepare for publication, Volume 43 (1933) following the plan of using the Committee on Publication of Proceedings as referees.

Membership. Chairman Andrews reported 45 applications for membership.

Press Secretary. Dr. Edington gave an account of the activities of his office and urged that members having papers to be read send him advance abstracts of their papers for the use of his publicity work.

Program Committee. Chairman Scott presented the printed program containing over 100 titles. The executive committee extended to him and his committee a vote of thanks.

Relation of Academy to State. No report.

Research Committee. Chairman Foley urged the encouragement of individual research and attempts to raise funds for support of research projects.

State Library. Chairman Coulter reported that the Academy Library is adequately housed and protected but at present inaccessible because of the moving of the State Library into the new library building.

Treasurer. Dr. Paul Weatherwax presented the following report:

RECEIPTS

Balance on hand January 31, 1933		$407.40
Dues and initiation fees collected		554.00
Received from A. A. A. S.		99.00
		$1,060.40

DISBURSEMENTS

Secretary	$29.50	
Treasurer	20.60	
Editor	165.57	
Program Committee	99.50	
Postage on Proceedings	81.26	
Academy Foundation	111.09	
Check Tax	.40	
		$507.92
Balance in bank		552.48
		$1,606.40

(Signed) PAUL WEATHERWAX, Treasurer.
JOHN B. DUTCHER, J. E. SWITZER } Auditors.

The Treasurer was authorized to use such funds as may be available and necessary to supplement the funds ordinarily available to the Editor for publication of proceedings.

Junior Academy of Science. Chairman Enders reported nine affiliated Junior Academy of Science organizations.

A. A. A. S. H. E. Enders, Academy Representative on the council of A. A. A. S., reported activities of the Academy Conference of which he was made Chairman. The campaign to have A. A. A. S. meetings in Indianapolis is progressing and there is good prospect of having these meetings in Indianapolis in 1937.

Nominating Committee. Chairman Davis reported the names of five members whom the Executive Committee recommended for election as Fellows. They are:

DR. A. R. BECHTEL, Wabash College.
DR. THEODOR JUST, University of Notre Dame.
DR. GEORGE SPITZER, Purdue University.
DR. E. R. SMITH, DePauw University.
DR. C. F. ADAMS, Indianapolis.

REPORTS OF SPECIAL COMMITTEES

Revision of Constitution. Report of committee was read and discussed at length and the specific recommendations referred to the General Session.

Anniversary. Chairman Edington reported progress of the plans for celebrating the 50th Anniversary Meeting of the Academy next year.

New Business. The following committee was appointed to receive invitations for the next annual meeting: W. E. Edington, E. G. Mahin and F. B. Wade.

E. G. Mahin and N. E. Pearson were appointed members of the resolutions committee.

Upon motion properly seconded and carried the President was instructed to appoint a committee to consider revision of the by-laws and report at the next annual meeting. (E. G. Mahin, F. B. Wade and R. C. Friesner were later appointed on this committee.)

MINUTES OF THE GENERAL SESSION

Following an address of welcome by President W. L. Bryan and response by President Lyon the minutes of the Executive Committee were read and approved. The recommendations of the Nominating Committee to the Executive Committee regarding Fellows was unanimously approved.

The proposed revision of the constitution was again read and referred for final action to the next annual meeting of the Academy.

The Academy gave a vote of thanks to S. A. Cain for his work as Editor. Upon motion properly seconded and carried the Editor was instructed to publish in the next volume of the Proceedings a bibliography of Barton W. Evermann's publications pertaining to Indiana. This is to be prepared by W. S. Blatchley.

At a brief business meeting following the annual dinner the following business was transacted: Chairman Mahin of the Resolutions Committee offered the following resolution which was unanimously adopted:

The Indiana Academy of Science, now assembled in its forty-ninth annual meeting, expresses, in this formal manner, the gratification which is individually felt by the membership, for the arrangements that have been made for our comfort and convenience, and which have contributed so materially to the success of the meeting. We desire especially to express our appreciation to the President of Indiana University for his gracious welcome, and to the Program Committee for its efficient planning of the events of the meeting.

W. E. Edington, Chairman of the Committee on Invitations, reported Indianapolis and Butler University as the place for the next annual meeting to be held during the last week in October or the first week in November.

Chairman Davis of the Nominating Committee made the following nominations for officers for the year 1933-34:

President, J. A. NIEUWLAND, University of Notre Dame
Vice-President, M. L. FISHER, Purdue University
Secretary, R. C. FRIESNER, Butler University
Assistant Secretary, W. P. MORGAN, Indiana Central College
Press Secretary, W. E. EDINGTON, DePauw University
Treasurer, PAUL WEATHERWAX, Indiana University
Editor, S. A. CAIN, Indiana University

These nominees were all unanimously elected.

RAY C. FRIESNER, *Secretary.*

MINUTES OF THE JUNIOR ACADEMY OF SCIENCE

The Indiana Junior Academy of Science met for its annual meeting, at Bloomington, October 14, 1933. The meeting was called to order by Frank B. Wade, temporary president.

The following eight clubs were represented:

1. Hilltop Nature Study Club, North Madison.
2. Sciemus Club, Valparaiso.
3. General Science Club, Bloomington.
4. Biology Club, Crispus Attucks, Indianapolis.
5. Chemistry Club, Shortridge High School, Indianapolis.
6. Washington Center Hiking and Nature Lore Club, Whitley County.
7. Coesse's Hiking and Nature Club, Whitley County.
8. Science Club, West Lafayette.

PROGRAM

1. Film—Bananas: From Plantation to Ultimate Consumers—Dr. Enders
2. By request Dr. Enders showed the members the film of Leaf-cutting Ants of the Tropics
3. Whitley County Junior Academy's Trip to the Century of Progress—Dora Belle Dryer

4. Fossil Collecting in Whitley County—Robert Gates
5. Some migratory visitors to a Pine Woods in Jefferson County—illustrated with slides—John Kirkpatrick
   (Made by Soll Conn)
6. Birds—Bloomington Club
7. Glass—Shortridge—Walter Strong
8. Demonstration—Tom Thumb Engine, Valparaiso—Gerald Urshel

Five schools were represented with exhibits of pupil work. They were:

1. Washington Center Hiking and Nature Lore Club—Whitley County
2. Hilltop Nature Study Club—North Madison
3. Shortridge Chemistry Club—Indianapolis
4. General Science Club—Bloomington
5. Sciemus Club—Valparaiso

At the close of the program the following officers were chosen to serve during the year 1933-34:

M. M. WILLIAMS, President, Bloomington
C. E. RANSOM, Vice-President, Indianapolis
ANNA INSKEEP, Secretary, West Lafayette

EDNA BANTA, *Temporary Secretary.*

ERNEST DANGLADE

VEVAY, INDIANA
December 17, 1865

VEVAY, INDIANA
December 18, 1932

Ernest Danglade, son of Dr. T. M. and Sarah Pleasants Danglade, was born in Vevay, Indiana, on December 17, 1865.

While a young boy he suffered a fall from a horse, which permanently injured his back, but despite this physical handicap he carried on with a smile and made a decided success in life and many friends during his travels in every state in the Union.

When a small boy he seemed to show an interest in nature and science, and his quest for facts in this realm was never relinquished from this early date. He gathered vast stores of information which later were to prove useful to himself and to society. A bright mind and a wonderful memory were his valuable assets.

He was graduated from Vevay High School in 1885, and in 1889 graduated from Buchtel College, Akron, Ohio, with a major in chemistry. After teaching chemistry in the college for several years, he returned to Vevay to become Superintendent of Schools. About the year of 1908 he was appointed Scientific Assistant in the U. S. Bureau of Fisheries at Washington, and while there did valuable work for the Government as an expert on the fresh water mussel and other shell fishes. A few of his publications were: *The Mussel Fauna of Central and Northern Minnesota;* with C. B. Wilson. *Mussel Resources of the Illinois River; Conditions and Extent of the Natural Oyster Beds and Barren Bottoms of Lavaca Bay, Texas;* with H. F. Moore. *The Flat Worm as an Enemy of Florida Oysters.*

He made various travels for the Bureau of Fisheries and was for a while stationed at the Biological Station at Fairport, Iowa; he also made several trips in charge of the expedition aboard the U. S. S. Fish Hawk. He was a personal friend of the late Dr. Barton W. Evermann.

Ernest Danglade was an accomplished civil engineer, a mathematician, and spoke French and German fluently. He made several river trips with William Boepple, the German shell fish expert. He had a host of friends along all rivers he worked, including mussel fishermen and shanty boat men, all of whom were dear to him.

In 1916 he returned to Vevay to become County Superintendent of Schools, which position he held until his death on December 18, 1932. He was a member of the Indiana Academy of Science, the American Association for the Advancement of Science and the American Fisheries Society. He was a 32nd degree Mason.

He was never married. His survivors are a sister, Annette, and a brother, Emplen P. Danglade. Also two nephews, J. K. Danglade, Editor of the Vevay Reveille-Enterprise, and J. A. Danglade, at present Principal of the Vevay High School.

GERARD FOWKE (CHARLES MITCHELL SMITH)

MASON COUNTY, KENTUCKY
June 25, 1855

MADISON, INDIANA
March 5, 1933

Mr. Fowke's earlier boyhood was spent partly with relatives in Kentucky, but principally with his father until the death of the latter. He became a clerk and bookkeeper in Nashville, Tennessee, until 1873, when he returned to Kentucky. In the spring of 1876 he went to Illinois where he taught school for two years. He also taught school in Brown County, Ohio, and was principal of the grammar school at Sydney, Ohio.

In 1886 he reported upon the archaeology of the Monongahela Valley in western Pennsylvania. He also made studies in Ohio, Illinois and Kentucky. His archaeological investigations took him into many of the states of the Union and also led him into foreign lands. He visited Japan, and traveled for 700 miles down the Amur River, out into the Channel of Tartary, along the coast to the Okhotsk Sea in a search for the evidence of the migration of the American Indian from Eastern Asia.

Gerard Fowke was one who delighted in exploration and up to the last year of his life was active in wresting from Nature her secrets. During his long life there were no lengthy periods of inactivity.

He was a man who loved and was much beloved by children. He spent many hours with small groups of his little friends, revealing to them the story of the rocks, the streams and the plants.

Miss Hazel Hansford and W. N. Logan.

PUBLICATIONS BY GERARD FOWKE

1. A Sketch of Flint Ridge, in Licking County, Ohio. Smithsonian Rep., 1884, pp. 851-873.
2. Mounds in Pike County, Ohio. The Amer. Arch., 1898, pp. 62-68.
3. Prehistoric Mounds. Cincinnati Commercial-Gazette, July 22, 1888.
4. How a Mound Was Built. Science, August 10, 1888.
5. Some Popular Errors in Regard to Mound Builders and Indians. Ohio Arch. and Hist. Soc. Publ., Columbus, Vol. 11, March, 1889, pp. 514-533.
6. The Manufacture and Use of Aboriginal Stone Implements. Ohio Arch. and Hist. Soc. Publ., Vol. 11, March, 1889, pp. 514-533.
7. In Fort Ancient, by Warren K. Moorehead. Robert Clarke & Company, Cincinnati, 1890. Survey Notes of Fort Ancient, pp. 119-129; also portions of text.
8. In Primitive Man in Ohio, by Warren K. Moorehead. G. P. Putnam's Sons, New York, 1892.
   a. Flint Ridge, Licking County, Ohio, pp. 30-48.
   b. Excavations at Fort Ancient, pp. 84-90, 4 figures.
   c. Reports of Mounds Excavated in Ross County, Ohio, pp. 113-183, 15 figures.
9. Some Interesting Mounds. Amer. Anthropologist, Vol. 5, Jan., 1892, pp. 73-82.
10. Aboriginal Remains of the Piedmont and Valley Region of Virginia. Amer. Anthropologist, Vol. VI, No. 4, Oct., 1893, pp. 415-422.
11. Indiana Mound Riddles. St. Louis Globe Democrat, Dec. 3, 1893.
12. Some Prevalent Mistakes Concerning American Aborigines. Amer. Archaeologist (Moorehead), Feb., 1894, pp. 43-50.
13. Mounds in Pike County, Ohio. Proc. Philadelphia Acad. Nat. Sci., July, 1894, 5 figs.
14. Norse Remains in the Neighborhood of Boston Bay. Amer. Nat., July, 1894, pp. 623-625.
15. Cupstones. Amer. Archaeologist (Moorehead), Oct., 1894, pp. 315-316.
16. Recent Discoveries. Amer. Archaeologist "Discoveries" (Moorehead), Oct., 1894, p. 316.

17. Material for Aboriginal Stone Implements. Amer. Archaeologist (Moorehead), Nov., 1894, pp. 328-335.
18. Archeologic Investigations in the James and Potomac Valleys. Bur. Amer. Ethnology, Wash., Bul. 23, 1894, pp. 1-80, 17 figures.
19. The Archaeology of Ohio. Vol. VII, Part II, Geol. Surv., Ohio, 1894, pp. 1-55, 11 plates, 4 figures.
20. In the Twelfth Ann. Rep. Bur. Amer. Ethnology, Wash., 1894, are the following reports:
    a. Excavation of a Group of Mounds in Union County, Mississippi, pp. 267-278, 9 figures.
    b. Ancient Works near Dublin, Ohio, pp. 449-451, 1 figure.
    c. Mound Group on Hill Place in Brown County, Ohio, pp. 451-452, 1 figure.
    d. Stone Graves in Brown County, Ohio, pp. 452-457, 2 figures.
    e. Flint Quarries in Coshocton County, Ohio, pp. 457-458. Notes, Maps and Descriptions (with James D. Middleton) of Aboriginal Earthworks and Other Remains in Southern and Central Ohio, pp. 458-491, as follows: (f to o, inclusive).
    f. Works in Licking County, pp. 458-469, 5 plates, 11 figures.
    g. Stone Fort in Perry County, pp. 470-471, 1 figure.
    h. The Hopetown Works in Ross County, pp. 472-474, 2 plates.
    i. The Cedar Bank Works in Ross County, pp. 474-476.
    j. The High Bank Works in Ross County, pp. 476-479, 2 plates.
    k. The Liberty Township Works in Ross County, pp. 479-482, 1 plate, 1 figure.
    l. The Baum Works in Ross County, pp. 483-484, 1 plate.
    m. The Siep Works in Ross County, pp. 488-489.
    n. The Seal Township Works in Pike County, pp. 489-499, 1 figure.
    o. The Graded Way at Piketon, pp. 491-492.
    p. Explorations in the Valley of the Monongahela River, Pennsylvania, pp. 494-499, 1 figure.
    q. Earthwork in Warren County, Pennsylvania, p. 503, 1 figure.
    r. Enclosure on Rifle River, Michigan, pp. 516-518, 1 figure.
    s. Reconnaissance of the Upper and Lower Peninsulas (abstract), pp. 518-519.
21. Aboriginal Handicraft in Stone. Amer. Archaeologist (Moorehead), Feb., 1895, pp. 197-202.
22. The Uses of Stone Implements. Amer. Archaeologist (Moorehead), Apr., 1895, pp. 300-304.
23. Excavations in the Aboriginal Quarry Pits at Flint Ridge, Licking County, Ohio. Popular Sci., New York, Nov. and Dec., 1895.
24. Pre-Glacial and Glacial Drainage in Ross County, Ohio. Bul. Sci. Lab. Denison Univ., Granville, Ohio, Vol. IX, 1895, pp. 15-24, 1 map.
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26. The Equinoxes and History. Popular Sci., New York, September, 1896.
27. Stone Art. Thirteenth Ann. Rep. Bur. Amer. Ethnology, Wash., 1896, pp. 47-184, 278 figures.
28. Forests and Climate. Popular Sci., New York, March, 1897.
29. The Formation of Natural Bridges. Popular Sci., New York, March, 1897.
30. Pre-glacial Drainage in the Vicinity of Cincinnati, Ohio. Bul. Sci. Lab. Denison Univ., Granville, Ohio, Vol. II, Mar., 1898, pp. 1-10, 1 map. (This paper was printed subject to future corrections and additions.)
31. Archaeological Investigations on the Amur River, Siberia. Science, Vol. 9 (n. s.). No. 224, April 14, 1899, pp. 539-541.
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42. Abstract of work in Missouri and elsewhere in 1902-1906. American Anthropologist, Vol. 8, No. 3, Sept., 1906, pp. 533-537.
43. Superficial Deposits along the Mississippi. Proc. Ohio State Acad. Sci. (14th Ann. Report), Vol. 4, Part 7, pp. 349-352.
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    b. Work at Wyandotte Cave, Indiana, p. 91.
    c. Explorations at Flint Ridge, Licking County, Ohio, pp. 173-181, 2 maps.
    d. Flint Quarries and Workshops in Other Parts of Ohio, pp. 181-184.
    e. Aboriginal Flint Quarries in Southern Indiana, pp. 185-186.
    f. Aboriginal Flint Quarry in Missouri, p. 195.
    g. Aboriginal Iron Ore Mine in Missouri, pp. 266-267.
    h. Prehistoric Workshop near Lurey, Va., pp. 334-335.
53. Bureau of American Ethnology, Washington, Bulletin 76:
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    b. Report on Cave Explorotions in Other States.
    c. Examinations of Loess Reported to Contain Human Remains, in Northeast Kans. and Southeast Nebraska in 1914.
    d. Aboriginal House Mounds.
    e. Archaeological Work in Hawaii.
54. Bureau of American Ethnology, Washington, Annual Report, No. 44:
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    b. Excavations in Greenup County, Kentucky.
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        c1. The Shell Heap.
        c2. The Hog Island Mound.
        c3. The Flat-topped Mound.
        c4. Mounds near the Flat-topped Structure.
        c5. The Alexander Mound.
        c6. Other Mounds in Colbert and Lawrence Counties.
    d. Examination and Exploration of Mounds in Red River Valley, Louisiana.
        d1. Vicinity of Shreveport.
        d2. Vicinity of Natchitoches.
        d3. Vicinity of Alexandria.
        d4. Vicinity of Marksville.

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f. Archaeological Survey of Scott County, Arkansas.
g. Exploration of a Cave in Maries County, Missouri.
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i. The Elephant Beds of Kimmswick, Missouri.
j. The Mound and Salt Spring at Kimmswick, Missouri.
k. The Prehistoric Skeleton from Lansing, Kansas.
l. The Formation of Flint Deposits.
m. Flint Quarries in Coshocton County, Ohio.
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p. Flint Quarries in Carter County, Kentucky.
q. Flint Quarries in Todd County, Kentucky.
r. Flint Quarries in the Kanawha Valley, West Virginia.
s. Flint Quarries in Hardin and Wayne Counties, Tennessee.
t. Flint Quarries in Polk and Barton Counties, Missouri.
u. Flint Quarries in Jefferson County, Missouri.
v. Flint Deposits at Alton, Illinois.
w. Flint Quarries in Union County, Illinois.
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57. Perverted Benevolence as an Influence upon Racial Development. Proc. Ind. Acad. Sci., Vol. 37, 1927, pp. 73-79.
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EDWARD BRUCE WILLIAMSON

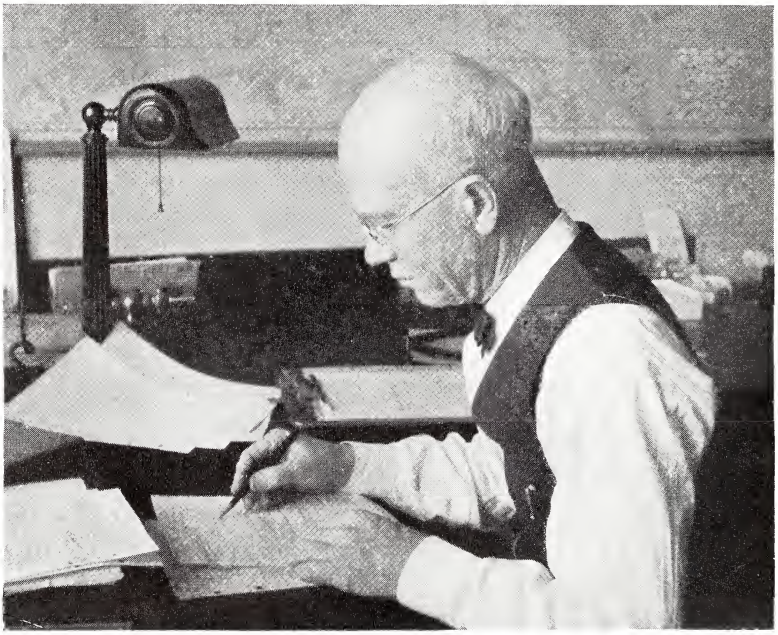
MARION, INDIANA — July 10, 1877
ANN ARBOR, MICHIGAN — February 28, 1933

Edward Bruce Williamson, prince among men, banker by vocation, and world authority on the dragonflies (Odonata) and a noted iris breeder, died at Ann Arbor, Michigan, February 28, 1933, at the age of fifty-five years and seven months, after an illness of nine days. His wife, Anna Tribolet Williamson, their foster daughters, Dorothea Thomas, Mary, and Jane, his brothers, D. K. Williamson of Bluffton, M. P. Williamson of Albuquerque, New Mexico, and sister, Mrs. Earl Merriam of Kansas City, survive him.

Bruce, as he was known to all of his associates, was born at Marion, Indiana, July 10, 1877. As a small boy he came with his family to Bluffton, and, excepting the winters of the past few years spent at Ann Arbor, Michigan, his entire life was spent as a resident of Bluffton or vicinity. After graduating from Ohio State University in 1898, he became assistant curator of insects in the Carnegie Museum at Pittsburgh, resigning that position a year later to accept a fellowship at Vanderbilt University for the year 1900-01. For one year he taught science in the high school at Salem, Ohio. Returning to Bluffton he succeeded his father as president of the Wells County Bank in 1905, which position he held until 1930. He acted as associate curator of the Odonata of the University of Michigan Museum of Zoology from 1916 to 1928 and as research associate in the same institution from 1928 till his death.

Williamson published his first scientific papers in 1898 and it was in this year too that he published his first papers on dragonflies, an order of insects in which he later became a world authority. During the next 35 years he published 123 scientific papers, 97 dealing with the Odonata, 5 on birds, 4 on fishes, 3 on crayfishes, one each on mammals, reptiles, and butterflies, and 11 of a miscellaneous nature.

Williamson described 14 new genera and 92 new species of dragonflies, as well as a new species of crayfish. His collection of dragonflies, including some 40,000 to 50,000 specimens and 310 types, and his large library dealing with the Odonata are deposited in the University of Michigan Museum of Zoology.



EDWARD BRUCE WILLIAMSON
Photo in March, 1932, by H. K. and L. K. Lloyd.

He became interested in the breeding of iris in 1906 and his first variety, Maude Tribolet, was announced in 1916, and one of his best known varieties, Lent A. Williamson, appeared in 1918. Beginning with 1925 he produced each year a number of new varieties which received the acclaim of iris fanciers. In all he produced 85 new varieties of iris. Mrs. Ethel Anson S. Peckham, writing of Williamson's irises in the July, 1933, Bulletin of the American Iris Society, comments as follows: "While compiling the list of Irises raised and introduced by Mr. Williamson, I cannot help thinking about their varied styles and characteristics. Perhaps no introducer has produced a greater range of color and shape, but Mr. Williamson did not confine himself to one section, even of a

group. He interested himself in trying to fill the needs of the real lover of Irises in gardens and of the landscape architect when he wished to plan an Iris garden that would have attractiveness and still grow and bloom well with little effort or expense."

A number of important collecting expeditions were made by Williamson, the more important ones as follows: Wyoming fossil fields for the Carnegie Museum in July and August, 1899; Central America, including British Honduras and Guatemala, January to March, 1905, for himself; Guatemala in June and July, 1909, with C. C. Deam; British Guiana, January to March, 1912, for himself; Colombia, December to March, 1916-17, in co-operation with the University of Michigan Museum of Zoology; and Venezuela and Trinidad, January to May, 1920, in co-operation with the University of Michigan Museum of Zoology. Several minor trips were made in various parts of the United States, his last one being an expedition to North Carolina, Georgia and Florida in August and September, 1932.

Perhaps Williamson's greatest achievements were made in Wells County, Indiana, and in particular in the Vanemon Swamp area, where for more than 30 years he studied intensively the dragonfly fauna year after year, a study which is unique and perhaps unequaled in the history of odonatology. He made innumerable notes and interpretations of his accurate and careful observations. His intimate knowledge of live dragonflies in the field enabled him to be a great collector and it is doubtful if any odonatist has ever even approximated him in the field. His achievements in his fields of interest have brought fame to the State of Indiana and to this Academy.

Bruce was endeared to each and everyone who had an association with him. He was outspoken in his beliefs and yet without enemies. He was always ready to assist those who deserved or called for assistance. From a close associate, Dr. Frederick M. Gaige, I have the following comment: "I did not know I could miss any man as I have E. B. He was the best loved man on our staff. Besides his value in every way to the Museum, he had been my most intimate friend for more than twenty years. His absence is still bewildering, too, for I cannot realize he will not be coming in soon. He was a grand fellow."

We have lost a valued friend and scientist, one who was president of the Indiana Academy of Science in the years 1918 and 1919, and a fellow in the Entomological Society of America. His multitude of friends and admirers will miss him but the memory of his energy, enthusiasm and generousness will forever remain with them as a happy remembrance.

Obituaries have been published in Science (April 7, 1933) and Bulletin of the American Iris Society (July, 1933). An obituary with a complete bibliography is to be published in the Annual Report of the University of Michigan Museum of Zoology for 1932-33.

J. J. DAVIS, *Purdue University.*

PRESIDENTIAL ADDRESS

ORIGINS OF INDIANA'S MAMMALS

Marcus Ward Lyon, Jr., South Bend

The origins of Indiana's mammals are not essentially different from the origins of many other elements of the Indiana biota, the mammalian portion of which is small, even when the fossil forms, all of Pleistocene Age, are included. In many respects these fossil species are more interesting than the recent mammals, either now extant or recently exterminated within historical times. A study of them reveals much of the past geologic history and climate of the state. Careful search of the literature, correspondence with those interested in mammals, and fairly intensive collecting yield no more than a total of 82 indigenous species of mammals in Indiana, 14 of which occur only in the fossil condition and usually as mere fragments. Future lucky efforts in collecting or fortunate paleontological finds might raise the number to a scant 100 species, but it is doubtful if the actual number will ever much exceed 85 or 90 species.

The 68 living and 14 extinct species of mammals are distributed among 11 (three extinct in Indiana) of the currently recognized (Weber) 18 orders of mammals (two of which orders are extinct). Twenty-two (six extinct in Indiana) of the 217 currently recognized families of mammals occur in the state; nearly half, 103 of these families, are extinct. These figures are more clearly brought out in tabular form, and in comparison with the total figures for the mammals of the world show how poorly the group Mammalia is represented in Indiana.

Number of Species of Mammals

	In Indiana		In the World	
	Total	Extinct	Total	Extinct
Species	82	14	15,000 ±	2,500 ±
Families	22	6	217	103
Orders	11	3	18	2

The figures for the orders, families and species vary within wide limits according to the ideas of different authors. The figures for Indiana approximate correctness, but do not include a few commonly recognized subspecies. The species figures for the world are only gross estimates.

The reasons for the paucity of mammalian forms of life in Indiana are several. First, Indiana does not lie in a general region where mammals are abundant either as to numbers or species. Second, the state is of comparatively small size and is without marked physiographic features, such as high mountain ranges, deserts, etc. The highest point

in the state is in Randolph County, about 1,285 feet above sea level, and the lowest point is the mouth of the Wabash, 313 feet, less than 1,000 feet in extremes of elevation. Third, nearly the whole of the state lies within one zoogeographic life zone or area, due in large part to the uniformity of climate throughout the state.

No discussion of the origins of Indiana's mammals will be intelligible without some mention of the zoogeographic areas of the world. These geographic areas have been established because of the similarity or homogeneity of the animals inhabiting them. Several different arrangements of the zoogeographic areas of the world have been proposed, but in the main they all resemble one another closely. The one followed here is the Sclater-Huxley system so ably set forth in Lydekker's Geographical History of Mammals.

Three major divisions ar recognized: 1. ARCTOGAEIC REALM embracing most of the world except South America and Australia and adjacent islands. This large ancient realm is subdivided into several smaller regions, only two of which concern us in this discussion: *Holarctic*, comprising the northern portions of each hemisphere and Africa north of the Desert of Sahara; and the *Sonoran*, practically the entire United States with the adjacent parts of Canada and the tablelands of Mexico. Indiana is situated within the Sonoran Region, although in the northern part of the state several Holarctic mammals are found. As would be expected, the origins of Indiana's mammals are in the main the same as the origins of the Sonoran mammals. A glance at a map shows the Sonoran to be intermediate geographically between the Holarctic to the north and Neogaea to the South, so that its mammalian fauna is a mixed one, though it contains numerous forms quite characteristic of it alone. 2. NOTOGAEIC REALM embracing Australia, and more or less remote islands. No mammals ever reached Indiana from this Realm. 3. NEOGAEIC REALM, without outstanding subdivisions, frequently termed the *Neotropical Region*, embracing all of South America, Central America, the low costal regions of Mexico and the West Indies.

Each one of these vast Realms and Regions may be subdivided into smaller areas, which are characterized by being inhabited by certain very definite types of mammals and the absence of others. In fact so characteristic are the assemblages of mammals in any one area, even though that be a very small one, that a competent mammalogist placed anywhere on the earth would be able to tell almost exactly where he was by making note of the mammals in that place, perhaps not with the same mathematical precision that a geographer can tell where he is, but with a precision that would probably astonish most geographers. As an example of this, one would tell he was in Indiana if he had but two distinctive species of its mammals: Franklin's Ground Squirrel of the northern part of the state and the Pennsylvania Cave Rat of the southern part. No other state possesses this combination. To be sure, if one is on foot, it may not seem like a very exact location to say one is in Indiana, but taking the world as a whole and realizing that Indiana is but a small spot on its surface, it places one's location rather exactly.

Not only are mammals distributed in two dimensions over the surface of the earth, but they have a third dimensional distribution as

well, being found in the earth at various depths and various geologic ages. As these geologic ages will be referred to occasionally farther on, it will not be out of place to list those that concern us in their chronologic sequence:

The later geologic periods and their subdivisions:

Quaternary Period. (Age of Man.) 500,000 to 1,000,000 years or more in duration	Recent. Pleistocene or Glacial.
Tertiary Period. (Age of Mammals.) Variously estimated 5,000,000 to about 20,000,000 years in duration.	Pliocene. Miocene. Oligocene. Eocene. Paleocene.

It is scarcely necessary to state that the lowest formations are the oldest and contain the more primitive types of mammals. In general the more recent the remains, the more they bear a stronger resemblance to the mammals of today, so that in the case of the Pleistocene mammals many of them are identical or practically so with living mammals.

No mammals are known in Indiana earlier than the Pleistocene which in point of geologic time is very recent. However, throughout the Tertiary times mammals existed in great abundance in western North America, and probably were found throughout Indiana and the eastern half of the continent, but conditions were not favorable for the preservation of their remains in the east and relatively little is known of them.

Throughout the whole of the Tertiary and Quaternary Periods North America had essentially the same form that it has today. At times it was broadly connected with South America, and at other times the two continents were widely separated and for considerable periods. At times it was united to northeastern Asia by a Bering Isthmus instead of being separated as at present by Bering Strait. This isthmus may have been of considerable width and have exhibited a polar climate in its northern part and a temperate climate in its southern part, thus admitting animals of two different climates to pass from one continent to the other. This land bridge is most important from the standpoint of the distribution of the mammalian life of the northern hemisphere, and accounts for the fact that the northern half of North America and the northern half of Eurasia constitute but a single zoogeographic region, the Holarctic. The evidence that northeastern North America together with Greenland and Iceland were united with northwestern Europe is less convincing, at least from the standpoint of the distribution of mammals.

These two land bridges served double purposes in that they also permitted the North American fauna to migrate into Eurasia and into South America. Like human travellers living away from home, a few of them migrated back again as much changed animals. At first thought one might think that these intercontinental routes would admit only a few mammals. No doubt it was only a few that passed over, but once

in a new pasture it is surprising to see with what rapidity a few migrants may multiply. Witness, in mammals, the spread of the European Rabbit in Australia, the European Hare in South America, and the well nigh universal distribution of the House Mouse and House Rat transported by human agency. Even the slow breeding horse spread from an introduced colony near Buenos Aires to the Straits of Magellan, a distance of some 10 to 12 hundred miles, in not quite half a century.

Owing to differences in temperature between the two Americas, north and south migrations were more difficult than the east and west ones between Eurasia and North America. It is extremely improbable that any animal passed from a marked degree of latitude to another with ease or without undergoing considerable change in its structure, unless the climate was changing at the same time, as during an advance or recession of a glacier. However, it should be appreciated in this connection that high altitudes of mountains are boreal in their climate, and that otherwise impossible migrations have occurred along mountain ranges from north to south.

Another interesting but much less important feature of the Tertiary continent of North America was the Mississippi Embayment, a shallow sound that extended up what is now the Mississippi Valley from the Gulf of Mexico to southern Illinois, sometimes present and at others absent. When one realizes that the mouth of the Wabash is only 313 feet above sea level, it is easy to understand what a slight subsidence of the continent would be needed to bring about a return of this arm of the Gulf of Mexico.

Perhaps the greatest geologic feature that affected the mammalian life of Indiana as well as other parts of North America and the world at large were the great glaciers that swept down from the north only to retreat and to return again. Two well marked glaciations are known for Indiana. The older, the Illinoian glaciation, has its southern limit of drift extending along the Ohio River westward to Jeffersonville, thence north to Brown and Monroe counties and thence southwesterly to Posey County, thus leaving a small roughly triangular area in southern Indiana that was uncovered by the glacier. The other and much more recent, the Wisconsin glaciation, has the southern border of its drift distributed irregularly across the state from Franklin County westward to Vigo County with a southern dip in Bartholomew County and a northern recession in Parke County. Between these two glaciations was an interglacial period during which time the climate was comparatively mild so that rather warm climated forms of mammals were found at least in the southern part of the state, and one even reached as far north as Wabash County. During the advance of a glaciation, Boreal mammals were pushed far to the south, so that such northern animals as Muskoxen were common throughout all of Indiana. With the retreat of the ice such animals followed it northward and invaders from the south came in where the ice had once been.

One of the most obvious facts of Indiana's mammals is that probably none of them are autochthonous, that is, none of them had their actual evolution within the state, but like ourselves they came from elsewhere. It is barely possible that one or two species of bats might

have had their evolution in caverns of unglaciated Indiana, but there is nothing that points clearly to such an origin. Indeed, nothing is more difficult to say than that such and such an animal had its origin at any particular place. In the present imperfect state of knowledge all that can be said is that such and such a mammal probably had its origin or underwent its evolution in such and such a general region and at a certain approximate geologic time. On the other hand, it is easy enough to say that certain particular animals did not have certain particular origins, where they are abundantly found, but that they are obvious migrants from some other region.

From the point of view of their origins Indiana's mammals may be grouped as follows:

1. Wide ranging autochthonous North American forms, for the most part peculiar to the New World, 43 species in 35 genera or subgenera.
2. Wide ranging autochthonous North American forms, peculiar to the New World, but of probable original Eurasian extraction, 11 species in 9 genera or subgenera.
3. Holarctic forms, always specifically distinct, but more or less closely related to or resembling Eurasian forms, 19 species in 15 genera or subgenera.
4. Forms of certain, probable or possible South American origin, 9 species in 8 genera.

These four groups are in no sense sharply delimited, and it has been a difficult matter to determine in which group certain forms should be placed and no doubt many will think the selection was done by the mere flip of a coin. A brief account of the members of each of these groups follows:

Wide Ranging North American genera, subgenera and species so far as known not having an origin or any immediate ancestors outside of this continent. It contains by far the largest number of Indiana mammals, genera or subgenera 35, species 43:

The Short-tailed Shrews *Cryptotis parva* and *Blarina brevicauda* are both widely distributed in North America, a few forms even reaching South America. Both occur throughout Indiana. They are closely allied to the genus *Sorex* of wide Holarctic distribution. Interestingly enough, both of the Short-tailed Shrews were first made known to science by that distinguished Indiana naturalist, Thomas Say, but not from Indiana specimens.

The twelve known Indiana species of bats are contained in seven genera. Four of the genera are quite peculiar to North America: *Lasiuris*, with two very distinct species, *Lasionycteris*, *Nycticeius*, *Corynorhinus*, each with but a single species. *Corynorhinus* is closely allied to the Old World genus *Plecotus*, but the other three are without close relatives anywhere. The other three genera of Indiana bats are: *Myotis*, with four characteristic North American species and one with obvious Eurasian affinities; *Pipistrellus* and *Eptesicus*, each with one species characteristically American. When and where Bats originated is unknown. They suddenly came to light in the Eocene and the earliest known

forms are fully developed bats. The Indiana species are all of a modern type. The Indiana species of *Myotis, Pipistrellus* and *Eptesicus*, probably evolved in North America, though they may have had a remote Eurasian ancestry. Two of the species of *Myotis, sodalis* and *grisescens*, have a center of distribution in the limestone caves of the Middle West, and may have had their origins in the same general region. They are probably the nearest approach to autochthonous species of mammals in Indiana.

The Raccoon, *Procyon lotor*, represents a family rather widely distributed in North and South America. Its only Old World member is the rare Panda of Asia. The family as a whole may have originated in Eurasia. It is well represented in the Recent Period of North and South America, and is found in the Pleistocene of each continent. The species is found throughout the state, probably entering from the south.

The Skunks seem to have originated in southern North America with one genus spreading into South America. At least southern North America is the seat of their distribution today. They do not seem to be known earlier than the North American Pleistocene. What appear to be rather distant relatives are found in the Ethiopian and Oriental Regions of the Old World. One species, the Eastern Skunk, *Mephitis nigra*, is common throughout Indiana, probably having entered the state from the east. The Prairie Skunk, *Mephitis mesomelas avia*, just enters the western border. The little Spotted Skunk, *Spilogale*, is much more southern in its habitat, and is found only in the extreme southwest corner of Indiana. Its admission to the state's fauna is open to question as no one as yet has procured a specimen.

The Badger, *Taxidea taxus*, is a genus peculiar to western and southwestern North America. It is rather closely allied to Eurasian forms, but is found fossil in the North American Pliocene and Pleistocene. It crosses the northern third or fourth of Indiana as an immediate invader from the west.

The Wolves, Foxes and allies constitute an old primitive group of carnivores; four genera with a total of five species occur or have occurred within Indiana, one as a probable Holarctic migrant. *Urocyon*, the Gray Foxes, is a wide spreading western and southern genus, probably entering Indiana from the south and west, and occurring at the present time throughout most of the state. The Prairie Wolf, *Canis latrans* (another species described by Thomas Say from material west of Indiana) has held its own against the march of civilization and is still found in fair numbers in the western and northern parts of the state, entering from the prairies of the west. The most interesting Canid of Indiana is the so-called Dire Wolf, *Aenocyon dirus*, known only from the Pleistocene of the Sonoran Region. The original specimen, a mere fragment of the upper jaw with a few posterior teeth, originally came from Pigeon Creek near Evansville, and was described as a new and very large species of extinct wolf by Joseph Leidy nearly 80 years ago. Subsequent explorations have found other remains, especially in the tar pits of Rancho LaBrea of southern California, and more recent studies have shown it to be not a true wolf, but to constitute a closely allied

genus. It probably was never found far north in Indiana, and evidently entered the state from the southwest.

The large group of Squirrels and allies has as a whole an uncertain origin. The group dates back to the Eocene of both northern hemispheres. With the exception of one genus, *Marmota*, the subgenera and species of Indiana's Sciuridae are most certainly all autochthonous in the Sonoran Region. The common Thirteen-striped Ground-squirrel, or so-called "gopher," *Citellus (Ictidomys) tridecemlineatus*, and the larger Gray or Franklin's Ground-squirrel, *Citellus (Ictidomys) franklinii*, had their development in the plains and prairies of the west and northwest and have entered Indiana from the northwest corner. The Striped Ground-squirrel has spread rapidly during historic times and has crossed the State of Indiana and gone about as far south as Indianapolis. Its larger gray cousin is spreading much less rapidly and is still confined to the northwest corner. The common Chipmunk, genus *Tamias*, probably originated in eastern or southeastern North America and appears to have entered the state from the eastern or southeastern border. It is found throughout Indiana. The three true or tree squirrels of Indiana are each placed in a separate subgenus and none so far as known have near relatives in other parts of the world, but are autochthonous in North America. They are: The Gray Squirrel, *Sciurus (Neosciurus) carolinensis*, in eastern or southeastern North America, formerly abundant in Indiana; the Fox Squirrel, *Sciurus (Guerlinguetus) niger rufiventer*, in southern United States, abundant throughout the whole of Indiana; the Red Squirrel or "Piney," *Scirus (Tamiasciurus) hudsonicus*, in northern North America, occurring in only the northern third of the state. The Fox Squirrel may have been an inhabitant of shores of the old Mississippi Embayment. The Flying Squirrel, *Glaucomys volans*, is peculiar to the eastern United States, having a distribution reminding one of that of the Chipmunk, the Gray Squirrel and the Fox Squirrel. Like the true squirrels the Flying Squirrels probably had an ancient origin in the Northern Hemisphere. The genus *Glaucomys* is probably a recently modified derivative from Eurasia.

The Pocket Gopher, *Geomys illinoensis*, is the sole Indiana representative of a superfamilial group of rodents characterized among other things by the possession of external cheek pouches. The group contains mouse-like forms, leaping forms and digging forms, of which the Pocket Gopher is an example. The group has had its origin and evolution in the west and southwestern Sonoran Region and is peculiarly a North American development. The ancestors run back to the Eocene and Oligocene, while the genus *Geomys* ranges from the Miocene to the present day. The Pocket Gopher is found in only the extreme northwest portion of the state and obviously entered from the plains and prairies of the west.

One of the most interesting of Indiana's mammals is the extinct Giant Beaver, *Castoroides ohioensis*. It is among the largest of rodents known, equaling in size a Black Bear. It evidently had its origin in the Pleistocene somewhere to the south of Indiana and as the last glaciation receded it followed northward. Its maximum distribution is in Indiana and all the finds have been referred to a period after the retreat of

the Wisconsin ice sheet. It is supposed to have had habits similar to those of the modern Beaver. Curiously enough it is represented in collections by much better material than the living Beaver so far as Indiana is concerned. Probably the best specimen unearthed came from Indiana and is in the collection of Earlham University.

The following seven species distributed in six genera or subgenera belong to a large group of rodents constituting the subfamily Cricetinae. It is a rather ancient group and may have had its origin in the North American Oligocene. It has spread remarkably, occurs abundantly throughout the Sonoran Region and the Neotropical Realm with an occasional form in Eurasia. Two species of White-footed Mice, *Peromyscus maniculatus bairdii*, and *Peromyscus leucopus*, are found in Indiana, both of them wide ranging species, though the subspecies *bairdii* is a prairie form from the west and probably was originally found only in primitive prairie regions of the state. With the cutting down of timber its range has been much extended. *Leucopus* is another one of those wide ranging species that probably originally came from the east. The Pennsylvania Cave Rat, *Neotoma pennsylvanica*, represents a genus of varied habits and habitat found in the southern and western United States; so far as known the single Indiana representative is confined to the limestone cliffs of Harrison County, the species evidently entering the state from the south or southeast. *Neotoma* is not represented in the Old World, nor did it enter South America. It is known from the Pleistocene of Pennsylvania. The Microtine division of the Cricetine Rodents has an uncertain place of origin, is widely distributed in Eurasia and North America, dating back to the Miocene. The common Meadowmouse, *Microtus (Microtus) pennsylvanicus*, is a wide ranging eastern species probably originally entering Indiana from the east. It is found throughout the state. The Prairie Meadowmouse, *Microtus (Pedomys) ochrogaster*, is apparently autochthonous on the prairies of North America and has entered Indiana on the west where it probably was originally confined, but has since extended its range throughout much of the state. The Pine Mouse, *Pitymys pinetorum*, is found throughout Indiana. The genus has a curious distribution: eastern United States, parts of Mexico, and central and southern Europe. It is probably an old type that early acquired fossorial habits. A related genus is found in Post-Pliocene cave deposits in Pennsylvania. The Muskrat, genus *Ondatra*, is the largest known microtine. It is a distinctive genus peculiar to nearly the whole of North America, from Boreal to to Lower Sonoran. Its wide distribution may indicate a rather ancient origin somewhere in North America; but on the other hand it may be a young genus of great adaptability and virility. Its spread in central Europe where a few individuals were set free is a beautiful example of how rapidly an introduced mammal may radiate.

The common Cottontail, genus *Sylvilagus*, found in every county of Indiana, is a representative of a wide ranging genus in America, mostly in the Sonoran and a few forms in South America. It is unknown in the Old World. It was possibly autochthonous in southwestern North America, at least the species are more numerous in the West. The Indiana species, *floridanus mearnsi*, is a wide ranging form.

The Peccaries, family Tayassuidae, are represented in Indiana by four finds of Pleistocene age; *Tayassu lenis*, fragments from an old cave near Williams, Lawrence County; *Mylohyus nasutus*, Gibson County; *Platygonus vetus*, Lawrence County, mere fragments; *Platygonus compressus*, Laketon, Wabash County. All of this material is lost. The Gibson County specimen is interesting in that the original description was based upon it. Fortunately it was well illustrated by Leidy. *Platygonus compressus* was a wide ranging species, fragments having been found in New York, the Mississippi Valley and probably Mexico. The Peccaries are a group of rather specialized Pigs having their whole development in North America, dating from the Oligocene and Miocene. Probably in comparatively recent times they entered South America. They naturally entered Indiana from the south or southwest, and at a time when the climate of the state was warmer than at present, probably in an early Pleistocene warm interglacial period.

The Solid-horned Muskox, genus *Symbos*, so far as known is found only in the Pleistocene of North America; perhaps its evolution and extinction all occurred in that period. It differs chiefly from the Common Muskox in that its horns formed a solid mass across the forehead. Its remains are widely scattered in North America from Mississippi to Alaska, more frequently (about seven times, mostly in the northern part), in Indiana than in any other state. It probably evolved just south of the glaciation and followed the ice northward when its retreated.

Twice fragments of Pleistocene Horses, genus *Equus*, have been found in Indiana. In neither specimen is the species determinable. Horses had practically their entire evolution in North America, whence they spread to Eurasia and Africa where they exist wild today. For some unknown cause they became extinct in America during the Pleistocene, although the climate of both North and South America today is well suited to them as shown by their rapid spread after introduction by man.

Wide ranging autochthonous North American forms for the most part peculiar to the New World, but of probable Eurasian extraction: 11 species in 9 genera or subgenera.

The Common Mole, genus *Scalopus*, of eastern United States is found throughout the whole of Indiana. It probably originated somewhere in the east and entered Indiana from that direction. It is a member of an old group dating back to the Miocene in North America. During the glaciation the Moles must have been pushed southward and then advanced on the retreat of the ice. The Star-nosed Mole, *Condylura*, is one of the rare mammals of Indiana, less than half a dozen specimens having been taken and none of them extant. It seems more northern in its distribution in the state. Whether it has entered Indiana from the northeast in recent times or has gradually worked its way northward after the last glaciation can only be a matter of conjecture.

The Fisher, *Martes pennanti*, is an indigenous animal of the colder parts of North America. It has been reported three times for Indiana, many years ago, and was undoubtedly a wanderer from the north, and can scarcely be considered to have been a normal inhabitant of the state.

The common Weasel, *Mustela noveboracensis*, is a member of a group of species common and indigenous to North America, and it is probably of comparatively recent Eurasian origin. Species of *Mustela*, however, are known from the Miocene of both North American and Europe.

The Lemming Mouse, *Synaptomys cooperi*, is one of Indiana's interesting mammals. The genus is usually regarded as Boreal, but it is found as far south in Indiana as Franklin and Lawrence counties. It may have had an autochthonous evolution in North America without Eurasian ancestry. A. B. Howell, the latest reviser of the genus, thinks it had a North American origin, evolving late in the Tertiary and possibly even in the Quaternary. It may not have been so strictly Boreal as at present. It must have been pushed south by the glaciation and in addition to following the retreating ice north, many adapted themselves to the warmer climate and have persisted till today. In the early days of Indiana mammalogy, Quick and Butler of Brookville had more specimens of this rare mouse in their possession than were in collections in all the rest of the world. They generously deposited specimens in the chief museums of Europe and America.

The Jumping Mouse, *Zapus hudsonius*, occurs throughout Indiana. It is of Pleistocene or Recent age in North America and usually is considered a rather Boreal animal. A closely related and apparently more generalized genus, *Eozapus*, occurs in China; elsewhere in Eurasia still more generalized *(Sicista)* and again much more highly specialized genera *(Dipus et al.)*, occur. *Zapus* is probably an invader of Indiana from the north.

Three species of Bison, or as they are more usually termed "Buffalo," have lived in Indiana. The most abundant, the plains Bison or Buffalo, *Bison bison bison*, occupying the western and southwestern part of the state in countless numbers a century and a half ago, and with possibly the Eastern Woods Bison, *Bison bison pennsylvanicus*, occupying the eastern and heavy timbered parts. A crude likeness of the Bison is on the great seal of the State of Indiana. No specimens from Indiana are known to be in collections. The other two species are extinct: *Bison antiquus*, represented by a fine skull from Knox County, in Earlham University, and *Bison latifrons* with no Indiana specimen. All three species had their evolution in America, but their ancestors undoubtedly came from Eurasia.

The Mastodon, *Mammut americanum*, because of its frequently found remains and large size, has been more often reported from Indiana than any other mammal. Fragmentary remains, mostly teeth, have been found from one end of the state to the other, and several almost perfect skeletons are known. It is an ancient type. Its remote ancestor was *Palaeomastodon* of the "Ur-Nile." Prof. Osborn estimates that to reach the forests of the Ohio and the Hudson it made a 10,000 mile journey via a northwest land connection, occupying in time 2,000,000 years. Remains of the Mastodon are not frequent in the Old World where the genus became extinct by the end of the Pliocene. Mastodons, however, were common in North America during the Pleistocene. That they persisted

until quite recent times is shown by an Indiana find, the grease from whose bones was used by workmen for oiling their shoes.

Holoarctic forms always specifically distinct, but more or less closely related to or resembling Eurasian forms; 19 species 15 genera or subgenera.

The true Shrews, *Sorex*, are represented in Indiana by two species. The genus is characteristically northern Holarctic and apparently had its origin in the Old World, crossing to North America comparatively recently, geologically speaking. *Sorex cinereus* is a northern form and entered the state from the north or followed up the last retreat of the glacier and still persists. *Sorex longirostris* is a species of the swamps of the southeastern United States and has probably entered Indiana from the south and east.

One bat, *Myotis lucifugus*, is the American counterpart of the Old World *Myotis daubentonii*, and undoubtedly developed in North America at a very recent date and has spread widely so that it is one of the commonest bats of the United States. Its antiquity in America is probably not much greater than that of the aboriginal Indians.

The Least Weasel, *Mustela rixosa*, the smallest carnivorous mammal in the world, is a member of a compact Holarctic group of the genus, usually northern in its distribution or living on high mountains. It has an almost continuous circumpolar or near-circumpolar distribution, and is probably found throughout the northern third of Indiana. The first of the three known Indiana specimens was taken only six years ago by our late lamented member, Bruce Williamson. That large aquatic weasel, the Mink, *Mustela vison*, has a close counterpart in Eurasia, *Mustela lutreola*, from which the American animal is probably a more or less remote derivative.

The Otter, *Lutra canadensis*, appears to be closely related to the Otter of Europe. According to Pohle, it crossed the land bridge between Eurasia and America in the Pliocene, retreating south during the glaciations and then re-establishing itself in the north. It is another of those wide ranging species which may have entered Indiana from any angle. The subspecies that used to occur throughout the state may possibly be *lataxina* of the southeast.

The circumpolar Wolverine was in America during the Pleistocene, probably a recent arrival from Eurasia. Its occurrence in Indiana, based on two scant records, can only be considered in the light of a straggler from the north.

The Black Bear, *Euarctos americanus*, is widely distributed in eastern North America with more or less close relatives in the western portion, and a closely allied species in Japan and eastern Asia. The Black Bear was a late Pleistocene or Pliocene arrival into American from Eurasia. Once across, it seeems to have spread rapidly. Scarcely more than 100 years ago it was common throughout all of Indiana.

The Red Foxes, *Vulpes fulvus*, of America are probably recent Eurasian immigrants. The Red Fox of Indiana according to all observations entered the state within historic times from the east. There is some question as to whether this Fox of the eastern United States is

an indigenous mammal or one artificially imported by man for the sport of fox-hunting and allowed to escape. It is a curious fact that in the Pleistocene deposits of the eastern United States no remains of this fox have been found, while bones of the Gray Fox, *Urocyon*, are of not infrequent occurrence. The Red Foxes of the north and west are certainly not human importations. The True Wolf, *Canis nubilus*, another species described by Thomas Say, appears to be closely related to the Wolves of Eurasia, and was probably derived from comparatively recent migrants by way of Bering Isthmus. It was once common throughout Indiana. The only scientific detailed description of an Indiana Wolf is that by the Prince of Wied, and the only known specimen is a skull collected by him near New Harmony 100 years ago the past winter. This skull is now in the American Museum of Natural History, New York.

Two species of the genus *Lynx* are reported for Indiana in the days that have gone. The Bobcat, *Lynx rufus*, appears to have been common throughout the state and only recently became extinct. A wretched mounted and antique specimen of it is in a collection of "curios" in a pool room at Royal Center, Cass County. There are some in the audience who probably have seen the Bobcat in its wild state in Indiana. A detailed description of this species is given by the Prince of Wied. The occurrence of the Canada Lynx within Indiana is less certain. Authors refer to it as having been found in the northern part of the state. The genus *Lynx* is a segregate of the large old genus *Felis*. The original home of *Lynx* appears to be Eurasia, and it is probably a rather recent immigrant. The Bobcat is a rather southern species, while the Canada Lynx is Boreal.

Man is the most recent of the indigenous mammals to have entered Indiana. According to Hrdlicka and others, *Homo sapiens americanus* most certainly reached America by way of Bering Isthmus, or more probably by Bering Strait, passing over from Asia in good weather in seaworthy boats of skin. As to whether man was in America during the Pleistocene is an open controversy, some contending that he was here during the Ice Age, and others only after its disappearance, placing his arrival at no more than 10 to 15 thousand years ago. If the latter is the case, it is an excellent illustration of the rapid spread of a mammal throughout a vast expanse of territory and the rapid development of astonishing degrees of human culture in a short period of time. Man may have been coexistent in America with such disappearing animals as the Mastodon, but if so, it is curious that no reference to such a characteristic animal is made in any human documents comparable to the carvings found in Europe, or to the pictures inscribed on cavern walls by the men of the Stone Age.

The Woodchuck or Ground Hog, *Marmota monax*, is a member of a Holarctic genus ranging eastward from the Alps to the Atlantic seaboard of North America. It is a recent type, making its first appearance in both continents during the Pleistocene. Its geographic distribution reminds one of that of the species of Chipmunk and Flying Squirrel found in Indiana. Whether it originated in eastern North America or is a comparatively recent migrant from Asia is only a matter of con-

jecture. Subspecies of *Marmota monax* are found in Alaska and elsewhere in northwestern North America.

The Beaver, *Castor canadensis*, is a representative Holarctic genus of wide distribution in the northern portion of both hemispheres. Fossil related members of the family occur from the Oligocene in America and from the Miocene in Europe. The genus *Castor* dates from the European Pliocene and the American Pleistocene, so it may be a comparatively recent arrival from the Eurasian Holarctic. It was once found throughout the whole of Indiana.

The Elk, *Cervus canadensis*, is a late migrant from Eurasia across the Bering Isthmus. It is not found in North America prior to the Pleistocene. It was widely distributed in Indiana in historic times and is the "Stag" of the early explorers. A closely related species is found in Asia.

The true Muskox, *Ovibos*, now confined in the living state to extreme northern North America and to Greenland, once had an extensive Pleistocene distribution in Europe, Asia and North America. It is not improbable that the genus may have had its origin in North America and thence spread westward. Its southern limit of distribution in North America closely corresponds with the southern border of the great ice sheets. As the glacier retreated, the Muskox followed northward. Only a single find of *Ovibos* is known from Indiana, while its relative, the extinct genus *Symbos*, is represented by several excellent remains.

That true Elephants, *Elephas* (or very closely allied genera), ever inhabited Indiana and in no small numbers may surprise many. Two species are currently recognized, but authorities do not agree on the identification of the Indiana remains. Each of two particularly good Indiana specimens have been made the type of a new species and a new subspecies. One form was long identified as the Old World Mammoth, *Elephas primigenius*, an animal well known to the old Cave Men of Europe and figured on ivory or painted on the walls of their caverns. Whether the Mammoth was contemporaneous with Man in North America is unknown. Both species were most certainly coexistent with the Mastodon, but much less numerous than the latter animal. The Jeffersonian Mammoth, *Parelephas jeffersonii*, typified by a beautiful specimen in the American Museum of Natural History, found in Grant County, is considered by Osborn (1925) to be an inhabitant of temperature climates and to have entered North America during the middle period of the Age of Man. The Woolly Mammoth, *Mammonteus primigenius* of the Old World, an animal of colder climate, is typified in Indiana by an adult female skull from Rochester, Fulton County. This specimen, also in the American Museum of Natural History, is the type of the subspecies *compressus*. It entered North America during the period of the last great glaciation. In point of size the Imperial Mammoth of America (not found in Indiana) had a height of 13 feet, 6 inches; the African Elephant of today has a height of 11 feet, 4 inches; the Jeffersonian Mammoth of Indiana, 10 feet, 6 inches; the Indian Elephant, 10 feet; the American Mastodon, 9 feet, 6 inches; the Woolly Mammoth, 9 feet, 3 inches.

INDIANA MAMMALS OF A DISTINCTLY SOUTHERN ASPECT, SOME OF THEM AT LEAST CERTAINLY FROM SOUTH AMERICA; 9 SPECIES, 8 GENERA.

The common Virginia Opossum, *Didelphis virginiana*, is in many respects Indiana's most interesting mammal. It is the most primitive of our mammals, being a Marsupial and not a Placental, and is a living representative of bygone ages. It differs more from the other mammals of the state than any of them differ from each other. Related forms are found as far back as the Cretaceous of Wyoming. *Didelphis* itself dates from the Eocene of North America, and is found in Europe from the Upper Eocene to Lower Miocene. At the present time the Opossums are characteristically South American, and it is more than probable that the animal originally evolved in North America, spread to the continent to the south, and then came north again. Opossums seem to be slowly spreading northward and becoming more common; they appear to have been in northern Indiana from the earliest historical times.

The great Cat, *Felis "concolor,"* variously called Cougar, Puma, Panther, Painter, Mountain Lion, has a range from Canada to Patagonia. The particular species formerly found throughout all of Indiana is designated technically as *Felis couguar*. Its past history is shrouded in mystery, as is that of most cats. The family Felidae is most abundant in the Old World and in the tropics. It is not unnatural therefore to think that the Puma may have had an origin in the warmer climates of the south and gradually to have spread in both directions into the south and north temperate zones. There is no evidence that it had an immediate origin in Eurasia, or in North America. *Felis* in the broad sense first dates from the Miocene of Europe.

The Rice Rat, *Oryzomys palustris*, recorded from Indiana on insufficient evidence, represents a cricetine genus with headquarters in the Neotropical Region. It occurs along the coastal regions of the southern and eastern United States and northward in the interior to Kansas and southern Illinois. It gives the impression of having been a recent invader from South America, but that continent originally received its cricetine rodents from North America in the distant past.

In the central United States the Canada Porcupine, *Erethizon dorsatum*, formerly ranged from the Ohio River northward into Canada, thus embracing the whole of Indiana. It was exterminated in the state within historic times and two examples from Laporte County are said to be in the State Museum. It is representative of a large group of peculiar Rodents, the Hystricoid, or Porcupine-like, found almost exclusively in South America. The group as a whole is of ancient lineage, rapidly disappeared elsewhere, but persisted in great variety and numbers in South America. The family Erethizontidae contains four extinct genera in addition to the living *Erethizon*, and extends from the Oligocene to the Recent in South America. The Canada Porcupine probably followed up the last glaciation and has now adapted itself to the colder parts of North America far removed from its original Neotropical origin.

The Swamp Rabbit, *Sylvilagus (Tapeti) aquaticus*, has the same general origin as the ordinary Cottontail already referred to, but is

probably more tropical, whether from South America or the coastal region of Mexico is only conjecture. It evidently followed up the Mississippi-Ohio-Wabash system, or perhaps even the older Mississippi Embayment and has reached just the southern end of Indiana.

Deer, of the genus *Odocoileus* and related genera, have long been inhabitants of America. The original home of their ancestors in all likelihood was Eurasia, and they early reached North America and gradually spread southward and evolved into the modern genera. Whether the White-tailed Deer, *Odocoileus virginianus*, had its origin in tropical America and later spread northward is only conjecture. Certainly it is in no sense a Holarctic form or Holarctic derivative, but is a characteristic Sonoran genus and species. Remains identical with the modern genus and species are found in Pleistocene deposits in Indiana and elsewhere in the United States. Another species of the genus *Odocoileus*, Cope's *dolichopsis*, is known by two fragments from the Pleistocene of Indiana. The latest student of this so-called species thinks it may not even be *Odocoileus*.

The Tapirs are represented in Indiana by a single tooth from the banks of Pigeon Creek near Evansville, identified as *Tapirus haysii*. The Tapirs are an ancient group. Fossil forms first appear in the Lower Eocene of Europe and North America, continue into the Pliocene, but in the Pleistocene are found only in eastern Asia and America, and in Recent times only in Malaya and South America. Whether *Tapirus haysii* underwent its development in the southern United States or is a comparatively recent invader from South America is only a matter of conjecture.

Jefferson's Ground-sloth, *Megalonyx jeffersonii*, is quite as interesting a mammal as the Virginia Opossum. It is another sole representative in Indiana of a peculiar and ancient order of mammals, the Xenarthra, an order occurring nowhere but in South America and the adjacent portions of North America where a few forms wandered in over the Central American land bridge, and, as in this instance, developed into independent genera and species. Most members of the order are extinct. Jefferson's Ground-sloth is represented in Indiana by but a single claw bone from Pigeon Creek near Evansville. The species as a whole is well known, the animal was of huge, clumsy proportions, perhaps about half the size of the Elephant. It was strictly vegetarian, pushing down trees by its great weight, or uprooting them with its strong claws. It was given the generic name *Megalonyx* by President Jefferson under the misapprehension that the huge claws came from a monstrous lion. The species was subsequently named for Jefferson himself by the French mammalogist, Desmarest.

Indiana's 82 species of living and extinct mammals have been shown to have had varied origins. Many had their evolution in the zoogeographic region of which Indiana is a part, many came from Eurasia by way of a Bering Isthmus, others came directly or indirectly from South America. None seems to have entered from western Europe or from Africa. They range from ancient primitive types, the opossum, existing today, to what is perhaps one of the latest evolved species

though of a generalized type, man himself, who has become the dominant figure in the world of mammals, and is rapidly exterminating the other mammals which are, zoologically at least, much more interesting. In size they vary from the small Shrew, less than one's little finger, to nearly the largest Elephants.

Arranging Indiana's mammals in a more or less modern geographic sense, about 30 per cent of them are northern forms, about 15 per cent are eastern or southeastern United States forms; about another 30 per cent are southern types or of general southern derivation, while about 15 per cent or slightly more are clearly of western origin, and 10 per cent are such wide ranging North American forms that nothing can be said with any degree of definiteness as to how they entered Indiana.

Thanks are due to Dr. Remington Kellogg, Dr. C. Lewis Gazin, and Mr. William L. Engels for valuable criticisms and suggestions.

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PAPER FROM THE GENERAL PROGRAM

INDIRECT CONTRIBUTIONS TO THE PROMOTION OF SCIENCE

W. M. BLANCHARD, DePauw University

There have been many explanations offered to account for the distressing situation in which the world has found itself these past five or six years. From some quarters have come intimations, in fact, assertions, that all our troubles are to be attributed to the development and the applications of modern science.

From others have come more tolerant, less dogmatic statements, modest suggestions we might call them, that science has outrun its teammates, philosophy and religion, and as a consequence man has come into the possession of forces which he is unable to control, and which are destined to destroy both him and the world in which he lives. It is strongly hinted that there should be declared a moratorium on scientific research until developments in the fields of the humanistic studies should make it safe for man to be intrusted with more knowledge of the physical world.

However, since there has not yet developed a Mussolini, a Stalin, or a Hitler with such dictatorial powers as to be able to prohibit scientific progress, and since there are still quite a few individuals who feel that it is not too much knowledge but too much selfishness, not too much science but too little religion, genuine religion, that is at the foundation of our trouble, and since men of science not only have no desire whatever to hinder the progress of the social order, but on the other hand would gladly cooperate in any endeavor to speed this progress, the march of science goes steadily on and always to the ultimate enrichment and not to the impoverishment of the human race.

Testimony in support of this statement is found in the great interest taken by the country in the Century of Progress Exposition, in the enthusiasm manifested at the recent great meetings of men of science both in this country and across the sea, in the wide publicity given the reports and addresses at these scientific congresses by the great metropolitan papers here and abroad, and in our own state in particular by the large number of papers in the various branches of science appearing in the program of this meeting of our Academy.

The spirit of science will not die; it cannot be strangled; it is immortal; it is as eternal as the Creator whose handiwork this scientific spirit is ever seeking to know, to understand, to interpret to all mankind.

Now science grows both by direct and indirect contributions. He who goes forth with an inquiring mind, bent on the search for truth, who

carries on experiments with his own hands, records accurately observations made with his own eyes, discovers and establishes facts hitherto unknown—he is a direct contributor to the progress of science. He who plans or suggests researches for others, as do our professors in graduate schools and our directors of research laboratories, who assembles data, detects new relationships, envisions the intrinsic meanings in the phenomena of matter, of energy, of life, whose imagination directs him to hitherto unopened doors which he himself or others at his suggestion may open—he also is a direct contributor to the progress of science.

But established scientific knowledge has become so broad and so deep, its horizon has become so extended that any serious contribution to its further enlargement can be made only at considerable financial cost. Laboratories, libraries, implements and tools of intricate mechanism and expensive construction are absolutely essential for the successful prosecution of any significant scientific research.

Any man, therefore, who builds and equips a laboratory, establishes a library, endows a research foundation, provides research fellowships, or helps to increase the funds available for scientific investigations is an indirect contributor, but no less a contributor to the progress of science, a benefactor of mankind. We have had in this country not a few conspicuous men and women of this class, and a far larger number more modest in their gifts, unheralded and unsung, perhaps not even known to the public, who, nevertheless, are indirect contributors to the progress of science and worthy of our appreciation and remembrance.

But in this brief paper I have in mind indirect contributions of another kind. Most of us here are teachers, college teachers, high school teachers, some of us members of faculties in institutions labeled universities, but engaged for the most part in undergraduate work. Each of us would enjoy the thrill that comes from the public announcement of an important discovery by "Mr. So-and-So" (ourselves). We should find much satisfaction in seeing our name attached to some epoch making paper appearing in such and such a scientific journal, which accepts only papers of unusual merit. But few of us have the technical skill to surpass all others in the prosecution of some research requiring exceptional technique, few of us are gifted with the imagination to conceive of methods superior to those designed by all others working in the field. Furthermore, most of us are so loaded with routine teaching schedules, or with other duties equally as time-consuming, that we have little time left to carry on the long series of experiments, the many confirmatory repetitions, or the long hours for searching books and journals to establish priority, all of which is so essential as prerequisites for the preparation of any creditable scientific paper.

Is there nothing we can do to make at least an indirect contribution to the promotion of science? Some of us feel that there is much we can do. Promote the development of a potential scientist and we contribute to the development of science itself. What is it to be a teacher of science? Surely it is far more than being a purveyor of scientific knowledge. Undoubtedly there is a certain amount of satisfaction to be found in supplying this particular kind of pabulum to youthful minds. But

does what we give them really feed them, nourish them, add to their growth? Does it not too frequently give them mental indigestion? Do we not too often have the wrong idea about teaching? Is not real teaching a process of creating hunger rather than satisfying it, creating a thirst rather than quenching it? Or, using another figure, is it not the function of the true teacher to discover intellectual sparks and fan them into flame; or, again, to arrest for a moment purposeless youth and give it purposeful endeavor with the dynamic of a great inspiration?

Applying these ideas to the teaching of science, is it not the duty of every teacher of science to endeavor to detect every potential scientist within his keeping, and is it not his sacred privilege to assist to his utmost in bringing that embryo to maturity? And who is a scientist? Who but he who is making direct contributions to the advancement of science, making some contribution to its clearer interpretation, its more significant implications? Is not, therefore, he who contributes to the development of a true scientist at least an indirect contributor to the promotion of science itself? Need we feel, therefore, that we must apologize for being teachers, if we are teachers in the highest meaning of that word? Better an effective teacher than an ineffective scientist.

It is a great privilege to be a teacher who can discover latent creative scientific ability in others and give it encouragement, inspiration, and direction until it attains fruition, reaching that stage in which it is recognized as a creator of science, a contributor to human knowledge in the interpretation of science, a man of successful scientific research. Our Academy should and does foster the teaching of science in this high and holy sense, and many of the papers presented at these annual meetings are expressions of this effort to cultivate the scientific spirit in the hearts of students with whom we are associated in classroom and laboratory. In many cases, far more important than the papers we read here are the impressions that have been made upon and the stimuli that have been given to the students in our laboratories who have had some part in the preparation of the data upon which the papers are based. In many cases, of much more significance than our direct contributions to science are the indirect contributions we make as teachers in the discovery and nourishment of the vital embryos which will become the scientists of tomorrow.

I know a college teacher who lectures to beginning students in general chemistry and who spends many hours a week in the laboratory looking for embryonic chemists. When he finds one, he gives him considerable time and personal attention for the next three years. In consequence, this laboratory is represented by many able chemists and teachers of chemistry throughout the country. I know a teacher of physics whose upper classes are comparatively small, but who had the pleasure last June of having five of his former students take their doctor's degree in physics in five different universities extending across the country from Yale to Minnesota. I know a teacher of zoology who, at the close of each year, migrates to Woods Hole for the summer with four or five of his most promising junior students, who, largely at their own expense, spend the summer vacation in acquiring a taste for

zoological research. It is his way of placing the stamp of discovery on embryonic zoologists. In my vicinity there is a professor of botany who, with his associates, spends many hours a week in giving their students an insight into botanical research, and with gratifying results. Eight years ago there applied for admission at a certain university in my neighborhood a youth who stood at the bottom of a class of 365 high school graduates. The Committee on Admission hesitated to take him. What could there be in such a freshman worthy of consideration? However, he was given a trial, and he fell into the hands of the head of the geology department, who found in him an embryonic geologist. As a result, this young man took his doctor's degree last June in geology at Johns Hopkins University with both Phi Beta Kappa and Sigma Xi honors.

I feel that such statements as these should be made occasionally for the encouragement of teachers, and there are many of them, who are interested in science but whose research is largely in students rather than in subjects, whose publications of scientific papers may not bring them distinction, but the results of whose labors entitle them to recognition as at least indirect contributors to the promotion of science. Surely the effort to contribute something to the promotion of science is a worthy one.

I trust that you will pardon me for confirming this statement and closing this paper with a quotation from an address delivered recently to American chemists by the greatest organic chemist living today, Professor Richard Willstätter, of Munich. I wish that every teacher of science might catch the full import of these words:

"In twentieth-century Chicago, in A Century of Progress, we recognize better than anywhere else the significant dualism of spiritual and of scientific endeavor. Has mankind really progressed through the centuries in art, philosophy, morals, ethics, tolerance, humanity—in one word, in religion? It seems to me that each generation and each individual must start anew and develop in certain aspects its own ideas, its own standards, and its own faith. Thus the contrast between human nature and technical development is steadily increasing. I agree with Sarton, the historian of the exact sciences, when he writes: 'The acquisition and systematization of positive knowledge is the only human activity which is truly cumulative and progressive.' Constant and permanent progress is only achieved in science and its applications—industry and medicine. We all have thousands of great teachers and we ourselves contribute to the growth of the structure of fundamental and applied science to greater height. Oftentimes we may ask ourselves with severe scruples: Is mankind really becoming wiser, better, and nobler? Has the power of religion grown to render impossible hate and strife between races and nations? Let us wish that religion attains the goal of blessing mankind with love and peace. The ever increasing beauty and power of science are manifest. While I hinted at the contrast between the spiritual and the scientific, I strongly sense that which is common to both religion and science. Both are truly international, both serve in the end the common weal of mankind."

PAPERS FROM THE PROGRAM OF THE BOTANY AND BACTERIOLOGY SECTION

PLANTS NEW OR RARE TO INDIANA, XIX

CHAS. C. DEAM, Bluffton, Indiana

Specimens of all of the species reported in this paper are in the Deam Herbarium.

Juncus scirpoides Lam. Newton County, Aug. 30, 1916, no. 21,517. In a low, sandy, prairie habitat 9 miles north of Morocco. Whitley County, Sept. 11, 1916, no. 21,710. Low border of the southwest side of Blue River Lake.

Chenopodium missouriense Aellen. My specimens were named by Paul Aellen of Basle, Switzerland. Clay County, Sept. 21, 1932, no. 53,225. Roadside in Coalmont. Vermillion County, Sept. 19, 1932, no. 53,166. In a prairie habitat one and a half miles north and three-fourths of a mile west of Dana.

Anemone caroliniana Walt. This species was reported for Vigo County in 1897. Blatchley says it was collected by Miss Nora Arnold along the Durkey's Ferry road about five and a half miles north of Terre Haute. He adds that it was known to be there by Miss Arnold for, at least, 12 years. So far as I know Blatchley did not preserve specimens, at least, there was none in his herbarium which I bought. This year I asked Fred Donaghy of the State Normal School to visit the place and ascertain if it still persisted. On April 30, 1933, he found it to be common with *Ranunculus fascicularis* on a sand hill near the old Otter Creek school house and elsewhere.

Cladrastis lutea (Michx. f.) K. Koch. Brown County, Aug. 18, 1933, no. 54,279. This species was discovered by Messrs. Lewis and Zavitz of the Civilian Conservation Corps while working in the Brown County Game Preserve. The find was reported to me by T. E. Shaw, extension forester of the Purdue Agr. Exp. Sta., and he and I collected specimens on the above date. The tree from which we collected specimens is located in the north center of the Brown County Game Preserve on a slope and near the top of what is locally known as the Ogle Hollow. At this place there are several small trees, ¾ inches in diameter, and one large one about a foot in diameter, which is a snag about 9 feet high, the base being alive for about 4 feet and with numerous small branches. We were told that this species was found in adjacent hollows and that a former owner had cut one tree up into lumber. The tree is located in an area where black, white, and chestnut oak and hickory are the dominant species. The trees of this colony were an under story, growing on the steep slopes of both sides of the ravine with a remarkable variety of trees for this region. Within a radius of 50 feet the following species of trees were found: *Acer saccharum*,

Carya ovata, Carya glabra, Cornus florida, Fagus grandifolia, Fraxinus americana, Juglans cinerea, Ostrya virginiana, Quercus borealis var. *maxima, Quercus montana,* and *Tilia glabra.*

Callirhoë triangulata (Leavenw.) Gray. This species was reported by Scott McCoy in Hoosier Outdoors 13, no. 7, October, 1933. He writes that he found it "Aug. 14, 1932, growing in very sandy soil along the C. & E. I. Railroad about one mile north of Oaktown, Indiana." Since Hoosier Outdoors has a very limited circulation I am making this report. There is no specimen of this species in the Gray Herbarium or in New York Botanical Garden Herbarium.

Hydrocotyle americana L. Lagrange County, July 10, 1933, no. 54,090. A small colony was found in a clump of sphagnum moss among several small tamarack trees on the east side of Cogg Lake, which is half mile west of Oliver Lake or about 5 miles northwest of Wolcottville.

Aster exiguus (Fernald) Rydb. This is a segregate from *Aster ericoides* L. (*Aster multiflorus* Ait.) which I have from Benton, Jasper, Newton, Noble, Porter, Tipton, Vermillion, Warren, and White counties.

Aster ericoides L. (*Aster multiflorus* Ait.). Since this species and the preceding are an aggregate, it is best to give the distribution of the segregates. I have this species from Lake and Sullivan counties.

Aster oblongifolius var. *rigidulus* Gray. (*Aster Kumleini* Fries). This is a form of the species with an upwardly appressed pubescence. I have it only from Tippecanoe County where it is found in gravelly soil on the north side of Big Wea Creek where the creek is crossed by State Road 25.

Erigeron pusillus Nutt. Knox County, Aug. 28, 1915, no. 18,293, in very sandy soil along the railroad about 4 miles south of Vincennes. I found it here in 1933 and also on a sand hill along the railroad about a mile north of Oaktown.

Anaphalis margaritaceae (L.) B. & H. Elkhart County, Sept. 24, 1933, no. 54,645. A colony about 3 feet wide and 5 feet long in sandy soil, bordering a black and white oak woods on the south side of the road a mile and a half south of the Michigan line and about 6 miles northwest of Elkhart. It is to be noted that this species is strongly stoloniferous and odorless while *Gnaphalium obtusifolium* with which it is confused is an annual and has a strong characteristic odor. This species has been reported for various parts of the state but I believe all, at least, south of our northern border should be referred to *Gnaphalium obtusifolium.*

Hieracium longipilum Torr. St. Joseph County, Sept. 24, 1933, no. 54,666. Frequent in very sandy soil in a fallow field on the south side of the Anderson Road about a half mile west of the Elkhart County line or about 3 miles southeast of Granger. We have reports for this species in the state but this is the first authentic specimen I have seen.

NOTES ON INDIANA GRASSES, 1933

J. E. POTZGER, Butler University

This is the second contribution of a series of annual reports on Indiana grasses previously unreported for the counties specified. The nomenclature is that of Deam's Indiana Grasses, 1929.

The writer gratefully acknowledges the checking by Mr. C. C. Deam of the species listed. A specimen of each grass reported was deposited in the Butler University herbarium. Collections in Johnson County were made by Miss Hollis Jones of Bargersville.

Agropyron repens (L.) Beauvois. HENDRICKS COUNTY. One-half mile south of Royalton, edge of highway. STEUBEN COUNTY. Along edge of highway near Bass Lake.

Agrostis hiemalis (Walter) BSP. CLAY COUNTY. Five miles southwest of Poland. Open waste field. MARION COUNTY. Open waste field on Fort Harrison reservation. PUTNAM COUNTY. Along edge of woods one mile northeast of Darbytown.

Agrostis perennans (Walter) Tuckerman. JOHNSON COUNTY. Woodland near Center Grove high school, Bargersville. MORGAN COUNTY. Open upland woods along Sycamore Creek, four miles southwest of Centerton. MONROE COUNTY. Open woods, edge of fields, eight miles south of Bloomington.

Agrostis stolonifera var. *major*. (Gaudin) Farwell. FOUNTAIN COUNTY. Along edge of little creek, open woods. Four miles south of Veedersburg. HENDRICKS COUNTY. Along highway 40, near a ditch. Ten miles west of Plainfield. HANCOCK COUNTY. Along edge of pond on Reformatory grounds at Pendleton. JOHNSON COUNTY. Fields, meadows, roadsides near Bargersville. MARION COUNTY. Along edge of highway at Arlington Avenue near 33d St., Indianapolis. PUTNAM COUNTY. Along edge of Deer Creek four miles south of Manhattan.

Alopecurus ramosus Poiret. CLINTON COUNTY. Low muddy place in an old pasture. Twelve miles northwest of Lebanon.

Andropogon virginicus Linnaeus. CLARK COUNTY. Waste field, four miles west of Henryville. SULLIVAN COUNTY. Waste field in Shakamak Park.

Anthoxanthum odoratum Linnaeus. OWEN COUNTY. Along an open bluff, edge of open woods near upper Cataract Falls.

Aristida dichotoma Michaux. JEFFERSON COUNTY. Roadside, clay bank, seven miles west of Hanover. WASHINGTON COUNTY. Waste field, three miles south of Kossuth.

Aristida longespica Poiret. CLAY COUNTY. Old church yard about two miles northwest of Jasonville. JACKSON COUNTY. Waste field one mile south of Crothersville. SULLIVAN COUNTY. Waste field in Shakamak Park. VIGO COUNTY. Edge of woods two miles north of Farmersburg.

Aristida oligantha Michaux. PORTER COUNTY. Roadside above Mink Lake. SULLIVAN COUNTY. Waste field in Shakamak Park.

Arrhenatherum elatius (L.) Mertens and Koch. CLAY COUNTY. Along ditch near a country road, eight miles south of Manhattan.

Brachyelytrum erectum (Schreber) Beauvois. PUTNAM COUNTY. Shady moist upland woods, one mile northeast of Darbytown.

Bromus japonicus Thunberg. BOONE COUNTY. Edge of ditch near the highway, ten miles northwest of Lebanon.

Bromus incanus (Shear) Hitchcock. HAMILTON COUNTY. Upland mixed hardwoods, four miles south of Noblesville.

Bromus commutatus Schrader. MARION COUNTY. Along the highway two miles west of Millersville.

Bromus purgans Linnaeus. OWEN COUNTY. In crevices of rocks of shady upland woods above Upper Cataract Falls.

Bromus purgans forma *laevivaginatus* Wiegand. HAMILTON COUNTY. Upland mixed hardwoods, four miles south of Noblesville.

Bromus secalinus Linnaeus. TIPPECANOE COUNTY. Along an old road along Flint Creek, three miles west of West Point.

Bromus tectorum Linnaeus. JOHNSON COUNTY. Waste place along road near Bargersville.

Calamagrostis canadensis (Michaux) Beauvois. CLINTON COUNTY. Low place in open woodland along Road 52, seventeen miles northwest of Lebanon.

Cenchrus pauciflorus Bentham. OWEN COUNTY. Along roadside, four miles south of Paragon.

Cinna arundinacea Linnaeus. MORGAN COUNTY. Shady alluvial soil along Sycamore Creek, four miles southeast of Centerton.

Dactylis glomerata Linnaeus. OWEN COUNTY. In open field above Upper Cataract Falls.

Danthonia spicata (L.) Beauvois. MONTGOMERY COUNTY. Dry upland field near Darlington Marsh. PARKE COUNTY. Open waste place near highway along Roaring Creek, six miles north of Rockville. TIPPECANOE COUNTY. Dry upland oak grove, soil covered with moss and lichens. Three miles west of West Point, above Flint Creek.

Digitaria Ischaemum Schreber. CLAY COUNTY. Waste places about cabins in Shakamak Park. JACKSON COUNTY. Waste field three miles south of Crothersville. MORGAN COUNTY. Waste places along the road near Sycamore Creek, four miles southwest of Centerton. OWEN COUNTY. Roadside, four miles south of Paragon. SCOTT COUNTY. Waste places along road, one mile north of Austin. SWITZERLAND COUNTY. Roadside, two miles northwest of Vevay. VIGO COUNTY. Along old road through open woods, especially in depression areas, three miles north of Farmersburg.

Digitaria sanguinalis Scopoli. BARTHOLOMEW COUNTY. Waste place near a filling station, one mile south of Taylorsville. CLARK COUNTY. Edge of road, dry creek bed, four miles west of Henryville. CLAY COUNTY. Waste place about cabins, Shakamak Park. HENDRICKS COUNTY. Roadside along Highway 67, one mile southeast of Mooresville. JEFFERSON COUNTY. Clay bank along roadside, seven miles west of Hanover. OWEN COUNTY. Roadside, four miles south of Paragon.

Echinochloa crusgalli (L.) Beauvois. CLARK COUNTY. Along edge of little creek, four miles west of Henryville. MORGAN COUNTY. Allu-

vial soil along Sycamore Creek, four miles southwest of Centerton. SCOTT COUNTY. Waste places along road, one mile north of Austin. SULLIVAN COUNTY. Low wet ground along a pond near Sullivan.

Elymus canadensis Linnaeus. MARION COUNTY. Low waste place near 52d St. and Boulevard Place, Indianapolis. OWEN COUNTY. Hillside along the side of the road, edge of woods, four miles south of Paragon.

Elymus riparius Wieg. MORGAN COUNTY. Shady place along Sycamore Creek, alluvial soil, four miles southeast of Centerton.

Elymus striatus Wildenow. FOUNTAIN COUNTY. Upland near edge of woods, also along fences, four miles south of Veedersburg.

Elymus virginicus Linnaeus. CLAY COUNTY. Edge of lowland woods near Eel River, three miles northeast of Bowling Green. FOUNTAIN COUNTY. Lowland woods along edge of creek, four miles south of Veedersburg. GREENE COUNTY. Edge of ditch near Highway 67, three miles southwest of Worthington.

Elymus virginicus var. *glabriflorus* (Vasey) Bush. MARION COUNTY. Along a ditch, Keystone Ave. and 62d St., Indianapolis.

Eleusine indica (L.) Gaertner. JACKSON COUNTY. Waste place along roadside, one mile north of Seymour. JOHNSON COUNTY. Waste places near Bargersville. OWEN COUNTY. Roadside, four miles south of Paragon. SWITZERLAND COUNTY. Old road along edge of woods, one mile south of Pleasant.

Eragrostis capillaris (L.) Nees. JOHNSON COUNTY. Open woodland near Bargersville.

Eragrostis hypnoides (Lamarck) BSP. JOHNSON COUNTY. Open woodland near Bargersville.

Eragrostis cilianensis (Allioni) Link. BARTHOLOMEW COUNTY. Waste place near filling station, one mile south of Taylorsville. CLAY COUNTY. Waste place in Shakamak Park. GREENE COUNTY. Dry ditch along Highway 67, one mile southwest of Worthington. Sandy soil. HENDRICKS COUNTY. Roadside, one mile southeast of Mooresville. JACKSON COUNTY. Waste place along road, one mile north of Seymour. JOHNSON COUNTY. Waste places, old fields near Bargersville. MORGAN COUNTY. Roadside, four miles southwest of Martinsville. OWEN COUNTY. Roadside, four miles south of Paragon.

Eragrostis Frankii Steudel. CLAY COUNTY. Waste upland field in front of camp building in Shakamak Park. GREENE COUNTY. Dry sandy ditch along Highway 67, one mile southwest of Worthington. JOHNSON COUNTY. Open woods near Bargersville. MARION COUNTY. Edge of woodland road, old clay upland on Fort Harrison grounds. WHITE COUNTY. Roadside, waste places, one and one-half miles north of Monon.

Eragrostis pectinacea (Michaux) Nees. HENDRICKS COUNTY. Roadside along Highway 67, one mile southeast of Mooresville. JOHNSON COUNTY. Waste places about barnyard, Bargersville.

Eragrostis spectabilis (Pursh) Steudel. JOHNSON COUNTY. Roadside and open fields near Bargersville. LAPORTE COUNTY. Between railway tracks of old switch near Michigan City. OWEN COUNTY. Roadside, edge of Spencer city limits. SCOTT COUNTY. Waste places along road, one mile north of Austin. SULLIVAN COUNTY. Roadside near Pax-

ton. SWITZERLAND COUNTY. Old road along edge of woods, one mile south of Pleasant. VIGO COUNTY. Dry waste fields, two miles north of Farmersburg.

Festuca elatior Linnaeus. HENDRICKS COUNTY. Lowland along road, half mile east of Royalton. HANCOCK COUNTY. Along edge of pond on grounds of Pendleton Reformatory. JOHNSON COUNTY. Side of road, edges of fields near Bargersville. MARION COUNTY. Along highway near Johnson's Hill, two miles east of Millersville.

Festuca obtusa Sprengel. HAMILTON COUNTY. Shady upland woods near the Jose Dale estate.

Festuca ovina Linnaeus. OWEN COUNTY. Edge of woods on upland above Upper Cataract Falls.

Festuca octoflora Walter. OWEN COUNTY. Open hillside, waste fields above Upper Cataract Falls.

Glyceria striata (Lamarck) Hitchcock. CLAY COUNTY. Low wet place in lowland woods along Birch Creek, Ashboro. HAMILTON COUNTY. Low wet ground near the Jose Dale estate.

Hordeum jubatum Linnaeus. CLINTON COUNTY. Low muddy place in old hog pen, twelve miles northwest of Lebanon. TIPPECANOE COUNTY. Along roadside, one mile north of Clark's Hill.

Hystrix patula Moench. HAMILTON COUNTY. Upland mixed hardwoods, four miles south of Noblesville.

Leersia oryzoides (L.) Swartz. MORGAN COUNTY. Roadside ditch, four miles southwest of Martinsville.

Leersia virginica Wildenow. CLARK COUNTY. Waste places about old homes, especially shaded corners, three miles west of Henryville. CLAY COUNTY. Shady places along creeks, one and one-half miles northwest of Jasonville. MORGAN COUNTY. Alluvial soil along Sycamore Creek, four miles southwest of Centerton.

Lolium perenne Linnaeus. MARION COUNTY. Vacant lot on Capitol Ave. near 30th St., Indianapolis. OWEN COUNTY. Along edge of road in McCormick's Creek Park. SULLIVAN COUNTY. Roadside, half mile south of Sullivan.

Muhlenbergia mexicana (L.) Trinius. MORGAN COUNTY. Along edge of ditch along Highway 67, one mile southeast of Mooresville. MONTGOMERY COUNTY. In ditch on railway right-of-way, four miles north of Crawfordsville. RIPLEY COUNTY. In a ditch, one mile northwest of Versailles. SULLIVAN COUNTY. Edge of dry creek in lowland woods, three miles south of Hymera.

Muhlenbergia glabriflora Scribner. GREENE COUNTY. Edge of ditch in dense tangle of vegetation along Road 67, three miles northwest of Worthington.

Muhlenbergia Schreberi J. F. Gmelin. CLARK COUNTY. Waste places about old homes, three miles west of Henryville. PORTER COUNTY. Edge of road near lowland woods, Dunes Park.

Muhlenbergia sobolifera (Muhlenberg) Trinius. CLAY COUNTY. Upland woods near Shakamak Park.

Panicum capillare Linnaeus. BARTHOLOMEW COUNTY. Roadside embankment, one mile south of Taylorsville. CLARK COUNTY. Edge of creek, four miles west of Henryville. JOHNSON COUNTY. Waste places

along edge of road near Bargersville. MORGAN COUNTY. Waste place along road near Sycamore Creek, four miles southwest of Centerton.

Panicum dichotomiflorum Michaux. CLARK COUNTY. Along roadside, three miles west of Henryville. CLAY COUNTY. Old church yard, two miles northwest of Jasonville. OWEN COUNTY. Roadside, four miles south of Paragon. SCOTT COUNTY. Waste places along road, one mile north of Austin. STARKE COUNTY. Waste area along railway tracks, two miles north of San Pierre. VIGO COUNTY. Woodland road, four miles north of Farmersburg.

Panicum virgatum Linnaeus. CLAY COUNTY. Along railway tracks, four miles south of Worthington.

Panicum huachucae Ashe. FOUNTAIN COUNTY. Edge of woods, open fields, four miles south of Veedersburg. HENDRICKS COUNTY. Along edge of highway, four miles west of Lizton. HANCOCK COUNTY. Along edge of pond on grounds of Pendleton Reformatory. JEFFERSON COUNTY. Roadside bank, seven miles west of Hanover. MARION COUNTY. Low shady woods near 37th and Drexel Blvd., Indianapolis. OWEN COUNTY. Shady upland woods near Cataract Falls. STEUBEN COUNTY. Dry sandy upland woods, north shore of Fox Lake. TIPPECANOE COUNTY. Shady oak woods above Flint Creek, three miles west of West Point.

Panicum clandestinum Linnaeus. MARION COUNTY. In low ditch near Butler Botanical Garden, Indianapolis. PARKE COUNTY. Open waste place near Roaring Creek, six miles north of Rockville.

Panicum flexile (Gattinger) Scribner. TIPPECANOE COUNTY. Boggy soil, three miles west of West Point.

Panicum Gattingeri Nash. MARION COUNTY. In lowland between White River and canal, Butler grounds, Indianapolis. MORGAN COUNTY. Waste places along road near Sycamore Creek, four miles southwest of Centerton. SWITZERLAND COUNTY. Roadside, two miles northwest of Vevay. TIPPECANOE COUNTY. Waste area on floodplain of Flint Creek, three miles west of West Point.

Panicum lienarifolium Scribner. TIPPECANOE COUNTY. Shady upland woods above Flint Creek, three miles west of West Point.

Paspalum circulare Nash. JACKSON COUNTY. Waste field, one mile south of Crothersville. SULLIVAN COUNTY. Waste field in Shakamak Park.

Phalaris arundinacea Linnaeus. HENDRICKS COUNTY. Along Highway 40, ten miles west of Plainfield. MARION COUNTY. Along edge of ditch about two miles east of Millersville.

Phleum pratense Linnaeus. HANCOCK COUNTY. Open waste field near pond on Pendleton Reformatory. PARKE COUNTY. Edge of highway near Roaring Creek, six miles north of Rockville. HENDRICKS COUNTY. Along Road 40, ten miles west of Plainfield.

Phragmites communis Trinius. TIPPECANOE COUNTY. Bog near Flint Creek, three miles west of West Point.

Poa compressa Linnaeus. BOONE COUNTY. Edge of ditch near road, ten miles northwest of Lebanon. CLAY COUNTY. Along edges of field near the road, five miles southwest of Poland. FOUNTAIN COUNTY. Open woods near the road, four miles south of Veedersburg. HAMILTON

COUNTY. Open waste field near edge of woods, Jose Dale estate. JOHNSON COUNTY. Edges of fields, roadside, Bargersville. PARKE COUNTY. Along edge of highway near Roaring Creek, six miles north of Rockville.

Poa pratensis Linnaeus. HENDRICKS COUNTY. Lowland along road, half mile east of Royalton. HAMILTON COUNTY. Edge of woods in shady place, near Jose Dale estate. MONTGOMERY COUNTY. Field, on top of hill above Darlington marsh.

Poa sylvestris Gray. HAMILTON COUNTY. Dense shady woods near the Jose Dale estate.

Setaria lutescens (Weigel) Hubbard. BARTHOLOMEW COUNTY. Waste place near filling station, one mile south of Taylorsville. GREENE COUNTY. Railway right-of-way along Road 67, one mile south of Worthington. HENDRICKS COUNTY. Along side of highway 34, four miles west of Lizton. HAMILTON COUNTY. Waste place along Road 13, four miles south of Noblesville. JOHNSON COUNTY. Waste places, old fields, near Bargersville. MORGAN COUNTY. Waste places along road near Sycamore Creek, four miles southwest of Centerton. OWEN COUNTY. Roadside, four miles south of Paragon. PARKE COUNTY. Waste places about cabins in Shakamak Park. PORTER COUNTY. Roadside above Mink Lake. SCOTT COUNTY. Waste places along road, one mile north of Austin. SWITZERLAND COUNTY. Roadside, two miles northwest of Vevay. VIGO COUNTY. Roadside, two miles north of Farmersburg.

Setaria viridis (L.) Beauvois. HENDRICKS COUNTY. Roadside along Road 67, one mile southeast of Mooresville. JOHNSON COUNTY. Edge of road near Bargersville. OWEN COUNTY. Roadside, four miles south of Paragon. RIPLEY COUNTY. Roadside, one mile northwest of Versailles.

Sorghum halepense (L.) Persoon. CLAY COUNTY. Waste field on floodplain of Eel River, three miles northeast of Bowling Green. OWEN COUNTY. Cornfield in low place, four miles south of Paragon.

Sporobolus cryptandrus (Torrey) Gray. STARKE COUNTY. Waste sandy place along road, edge of San Pierre.

Sporobolus cryptandrus var. *involutus* Farwell. BENTON COUNTY. Sandy place (collection by Scott McCoy). LAPORTE COUNTY. Sandy soil along old railway switch, waste sandy places in general, east of Michigan City along Road 12.

Sporobolus vaginaeflorus (Torrey) Wood. MARION COUNTY. Edge of flower beds at home of John F. Cook, 5120 Broadway, Indianapolis. OWEN COUNTY. Sandy clay soil in road cut, about half mile northeast of Spencer.

Triodia flava (L.) Hitchcock. MORGAN COUNTY. Roadside along Road 67, one mile southeast of Mooresville.

Triplasis purpurea (Walt) Chapm. PORTER COUNTY. Sandy dune soil along old railway switch near Road 12 east of Michigan City.

Uniola latifolia Michaux. Shady lowland woods near Mill Creek, at Lower Cataract Falls.

ON MERTHIOLATE AND FUNGI ASSOCIATED WITH RINGWORM

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INTRODUCTION

During the latter part of the nineteenth century considerable confusion prevailed concerning the etiology of many kinds of human dermatitis. Insufficient descriptions of lesions and cases coupled with a confused terminology led to the merging of tinea, impetigo, and alopecia of various sorts into a mixed category. For example, "tinea" of the lips is probably rare at the present time and dermatitis of this area is usually of bacterial etiology, as has likely been true in the past.

By 1900 the mycotic skin conditions had begun to assume an entity separate from bacterial infections, in a large measure due to the work of Sabouraud, and an exact summary of the whole subject by this author[1] in 1910 further clarified the mycotic, as contrasted to bacterial, skin infections. Also it was recognized that fungi may infect any part of the human skin from the toes to the scalp. In any comprehensive bibliography of early fungus studies without doubt the names of Gruby, Bang, Whitfield, and Castellani would also occupy attention of the first order. We shall not attempt such a review, however.

In the last few years both clinical and laboratory studies[2 3 4 5 6] have dealt with the increasing prevalence of ringworm since the war, and the public health as well as medical problems presented by the increase and chronicity of this condition. The biology of the causative fungi has been dealt with in a comprehensive way by Weidman[3] and many recent studies have been made upon epidemiology, prevention, and treatment. Institutional attention to sanitation, involving the prevention of further spread of pathogenic fungi, and tests of many chemicals as agents of treatment have been the subjects of many reports.

Chemical agents suggested and used as agents of treatment have included salicylic acid, benzoic acid, phenol, menthol, thymol, volatile oils, iodine, silver nitrate, potassium permanganate, copper sulphate, zinc sulphate, zinc oxide, chrysarobin, calamine, sulphur, and thallium acetate. X-ray treatment has been used extensively. The British use of Whitfield's formula and the French use of tincture of iodine have been proverbial.

This laboratory in the last few years has examined the antiseptic action of the new mercurial, Merthiolate[7 8 9 10 11 12 13 14], from several points of view. This drug has been found to have, among other properties, high degrees of solubility in aqueous and protein media, a near absence of protein coagulation properties, very low toxicity for animals and humans, healing properties possibly due to sulphydryl, and adequate antibacterial properties. Buchsbaum and Bloom[15], on the basis of tests

against bacteria within living tissue cultures involving simultaneous antibacterial and anti-tissue effects, have reported a comparatively high value for Merthiolate. We have verified[16] this in tests of "white clot" or fibrin-containing media in which the physical conditions are somewhat similar to those found in infected tissues.

In view of the usefulness of Merthiolate as an antiseptic and its

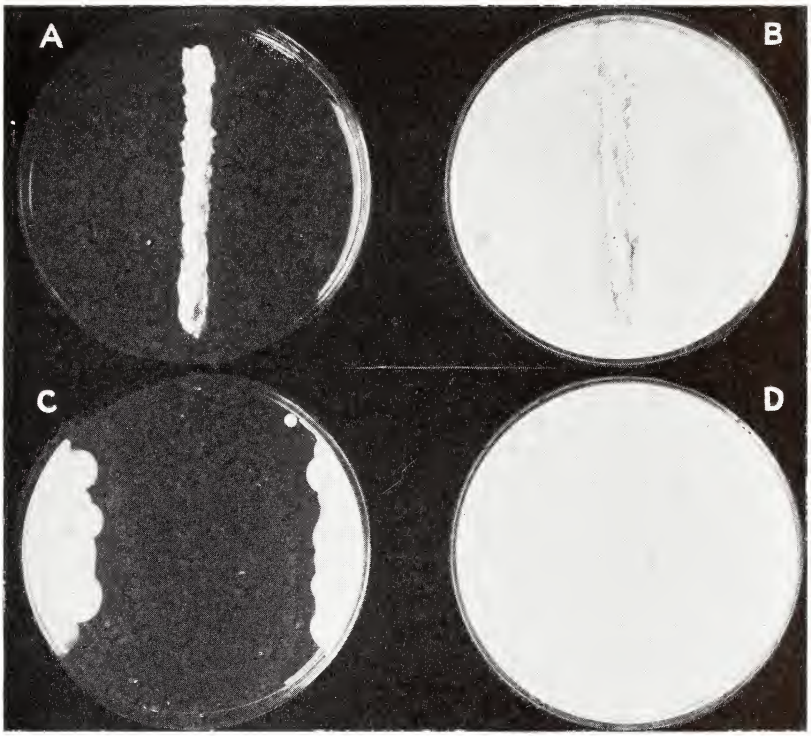

Fig. 1: *Trichophyton purpureum* No. 4183 Poured Agar Plates Prepared by Mixing 0.5 cc. Emulsion of Two Weeks Old Spore Containing Culture with 20 cc. Melted Agar, and, After Streaking with a Platinum Loop of the Indicated Materials, Incubating for Seven Days.

A. Merthiolate 1-1000 Cream, Containing Triethanolamine 1-80 and Carbitol 1-14.
B. Cream Base, Without Merthiolate, Containing Triethanolamine 1-80 and Carbitol 1-14.
C. Merthiolate Aqueous Solution 1-1000.
D. No Medication.

property of stimulating repair and healing it became of interest to examine the action of Merthiolate on pathogenic fungi.

Marshall[17] has reported that Merthiolate 1:10,000 kills *Trichophyton interdigitale* in five minutes but does not kill at a 1:100,000 dilution. Legge, Bonar, and Templeton[18] in an extensive comparative study showed that Merthiolate in all dilutions up to and including 1:10,000 killed all spores of *Trichophyton interdigitale* in five minute test exposures. In California they found this species more resistant to chemicals than *T. rosaceum.*

In this paper we shall present results of further tests of Merthiolate against pathogenic fungi, including the preparation of a cream vehicle which appears to bring about Merthiolate medication of the skin more adequately, and with more convenience, than may readily be done with liquids or solutions.

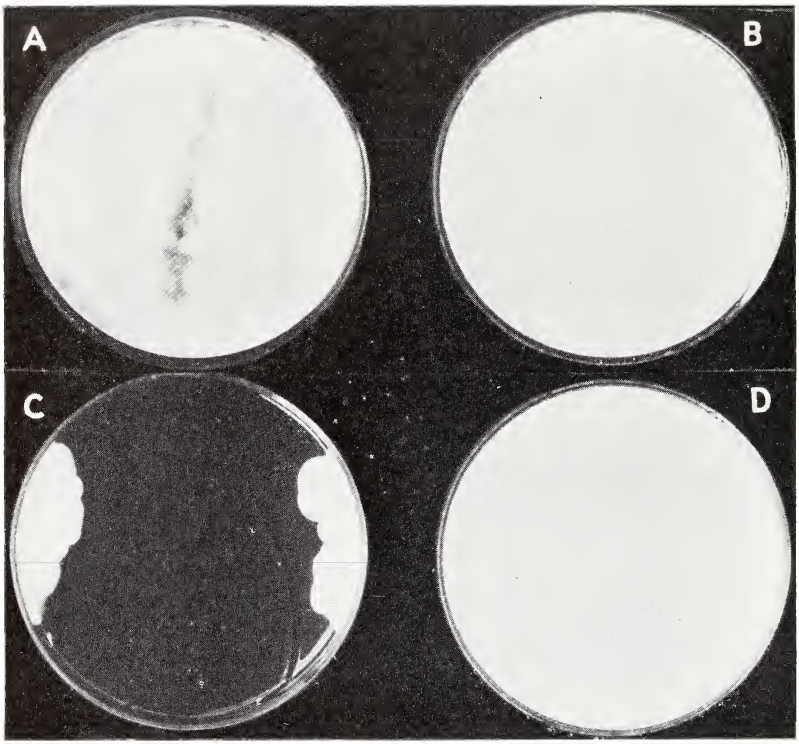

Fig. 2: *Trichophyton purpureum* No. 4183 Poured Agar Plates Prepared by Mixing 0.5 cc. Emulsion of Two Weeks Old Spore Containing Culture with 20 cc. Melted Agar, and, After Streaking with a Platinum Loop of the Indicated Materials, Incubating for Seven Days.

A. Triethanolamine Undiluted.

B. Carbitol Undiluted.

C. Merthiolate Aqueous Solution 1-1000 Containing Triethanolamine 1-80 and Carbitol 1-14.

D. No Medication.

EXPERIMENTAL

McCrea[19] has recently set forth a proposed standard method for the evaluation of fungicides. In preliminary test tubes tests of Merthiolate we have utilized these general test methods with certain modification as to volumes of test solutions. Instead of using 2 cc. volumes of chemical we prefer 5 cc. volumes which have been utilized in the F. D. A.[20] and other commonly used antibacterial laboratory procedures. Fungus test doses comprised 0.5 cc. taken from a 10 cc. water emulsion of a well spored agar slant of fungus culture. Medication of fungus

test doses with dilutions of chemical was conducted at 20° C. Ordinary platinum loop plantings of medicated spore culture were made after 5, 10, and 15 minute exposure intervals, to freshly melted deep-tube slants of glucose agar, which were incubated two weeks, then read. In McCrea's proposed standard method, the temperature of medication appears to have been omitted.

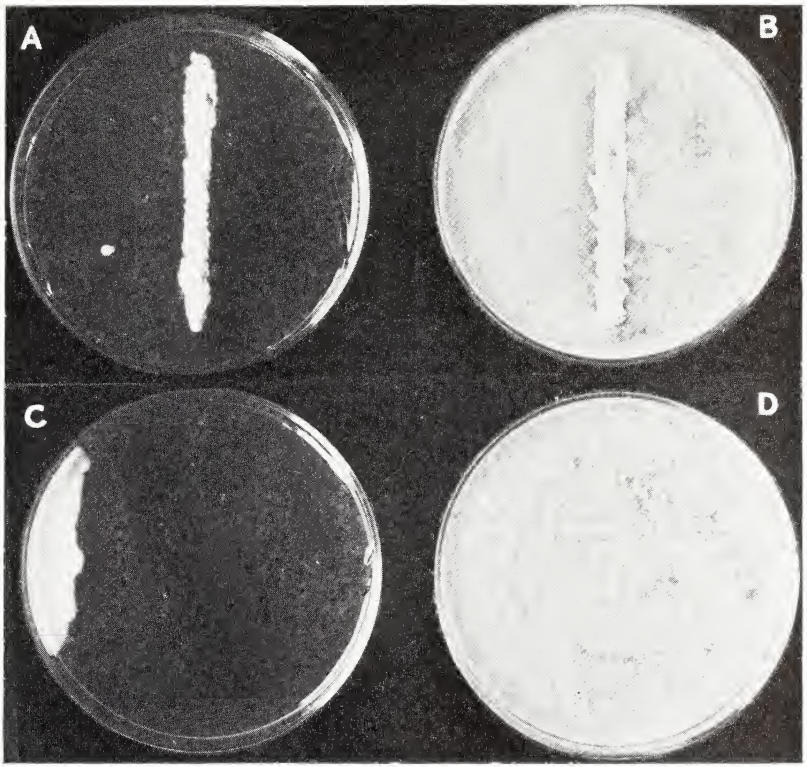

Fig. 3: *Epidermophyton rubrum* No. 655 Poured Agar Plates Prepared by Mixing 0.5 cc. Emulsion of Two Weeks Old Spore Containing Culture with 20 cc. Melted Agar, and, After Streaking with a Platinum Loop of the Indicated Materials, Incubating for Seven Days.

A. Merthiolate 1-1000 Cream, Containing Tricthanolamine 1-80 and Carbitol 1-14.
B. Cream Base, Without Merthiolate, Containing Tricthanolamine 1-80 and Carbitol 1-14.
C. Merthiolate Aqueous Solution 1-1000.
D. No Medication.

In order to make all preliminary experiments reproducible, three fungus test cultures were selected from the American Type Culture Collection. These were *Trichophyton purpureum* 4183, *Epidermophyton rubrum* 655. and *Microsporon lanosum* 650.

Fungicidal Action of Merthiolate in Aqueous Solution

Table I shows results of Merthiolate tests against the organisms just mentioned. It appears that in five minute exposures Merthiolate

in dilutions up to and including 1:10,000 is uniformly fungicidal for all three fungi. Merthiolate 1:20,000 is fungicidal for *Epidermophyton rubrum* and *Microsporon lanosum* only, while Merthiolate 1:40,000 is not effiective against any one of the three strains.

TABLE I

Test fungus	Trichophyton purpureum No. 4183			Epidermophyton rubrum No. 655			Microsporon lanosum No. 650		
Date tested	3-24-32			3-30-32			3-30-32		
Exposure of test culture to chemical (minutes)	5	10	15	5	10	15	5	10	15
Merthiolate 1:1000	—	—	—	—	—	—	—	—	—
5000	—	—	—	—	—	—	—	—	—
10,000	—	—	—	—	—	—	—	—	—
20,000	+	—	—	—	—	—	—	—	—
40,000	+	+	+	+	+	+	+	—	—
60,000	+	+	+	+	+	+	+	+	+
120,000	+	+	+	+	+	+	+	+	+

It may be mentioned that in these tests the plantings of medicated culture were made to deep tube slants of glucose agar, each containing about 25 cc. of culture medium, in order to eliminate growth inhibitory effects of any mercurial "carried over" with the inoculum. Some experimenters have occasionally resorted to the following alternative in order to distinguish lethal from inhibitory effects, namely replanting all negative medicated culture tubes with a second inoculum of non-medicated culture which in many instances might be many times the size of the medicated culture dose. It appears that the disadvantages of this procedure are obvious.

That the utilization of culture tubes containing a large amount of culture medium to dilute out the "carried over" chemical very highly is satisfactory is shown by the following experiment. A fungicidal test was conducted with three of the stronger dilutions of Merthiolate and *Trichophyton purpureum* 4183. The technique used was like that used

TABLE II

Test fungus	Trichophyton purpureum 4183					
Exposure of test culture to chemical (minutes)	5		10		15	
Culture Series	direct culture	sub-culture	direct culture	sub-culture	direct culture	sub-culture
Merthiolate 1:1000	—	—	—	—	—	—
2000	—	—	—	—	—	—
5000	—	—	—	—	—	—
Saline	+		+		+	

in the first tests, as recorded in Table I, except that the culture tubes upon which medicated culture was planted were subcultured to a further series of tubes of fresh media, and readings of both series of tubes made after two weeks' incubation. The results of this test are shown in Table II. The primary series of culture tubes, which had received medicated culture plantings directly, were negative as was shown to

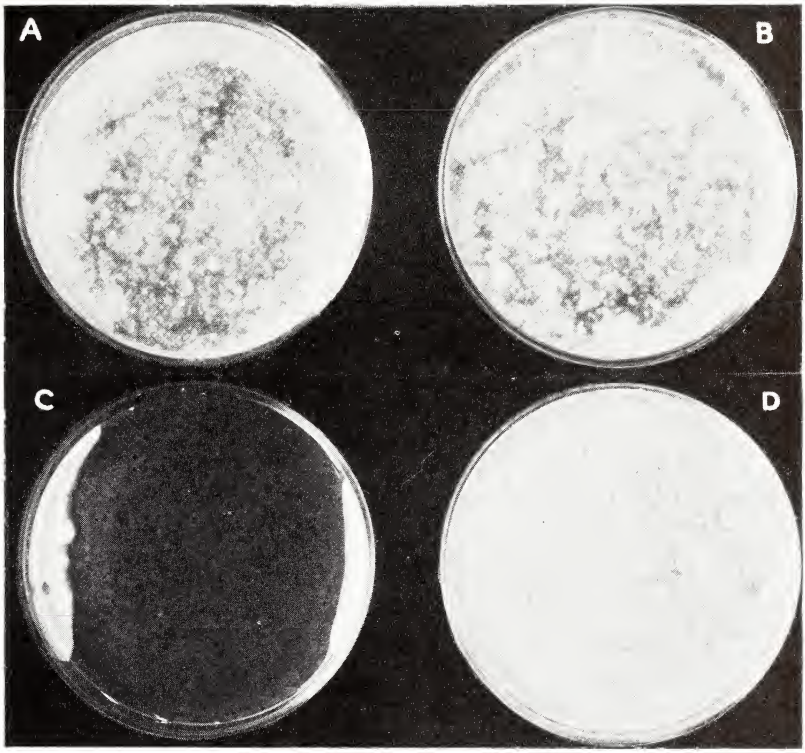

Fig. 4: *Epidermophyton rubrum* No. 655 Poured Agar Plates Prepared by Mixing 0.5 cc. Emulsion of Two Weeks Old Spore Containing Culture with 20 cc. Melted Agar, and, After Streaking with a Platinum Loop of the Indicated Materials, Incubating for Seven Days.

A. Triethanolamine Undiluted.

B. Carbitol Undiluted.

C. Merthiolate Aqueous Solution 1-1000 Containing Triethanolamine 1-80 and Carbitol 1-14.

D. No Medication.

be the case in Table I. Also the secondary series of culture tubes showed no growth, and this result appears to add certainty to primary culture readings.

The results set forth in Tables I and II verify those previously reported by Marshall,[17] and by Legge, Bonary, and Templeton[18] as referred to above, and show that Merthiolate in aqueous solution has ample "test-tube" fungicidal properties.

ACTION OF MERTHIOLATE IN A SPECIAL CREAM VCHICLE

In order to prepare Merthiolate in a form favoring better contact with infecting fungi in mycotic lesions of the skin for attempts at clinical use, due attention has been paid to the histology of the skin. The difficulties of adequate skin medication have been dealt with from the

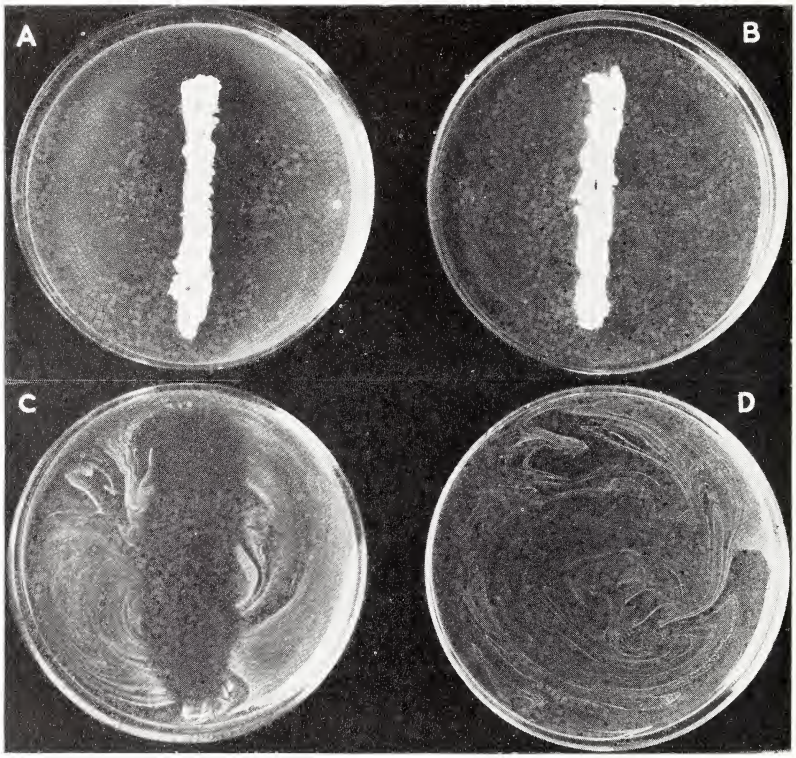

Fig. 5: *Staphylococcus aureus* Poured Agar Plates Prepared by Mixing 0.1 cc. Twenty-Four Hour Broth Culture with 20 cc. Melted Beef Extract Agar, and, After Streaking with a Platinum Loop of the Indicated Materials, Incubating at 37° C. for Twenty-Four Hours.

A. Merthiolate 1-1000 Cream, Containing Triethanolamine 1-80 and Carbitol 1-14.
B. Cream Base, Without Merthiolate, Containing Triethanolamine 1-80 and Carbitol 1-14.
C. Merthiolate Aqueous Solution 1-1000.
D. No Medication.

standpoint of overcoming the "insulating" effect of skin secretions and deposits through use of better oil-cutting accessory substances, and softening materials for horny layers.

Attention was directed[21] to certain unique properties of stearic acid cream vehicles or bases prepared with triethanolamine and carbitol, including excellent skin-softening and natural skin oil emulsification properties.

FUNGICIDAL TESTS OF SOLUTIONS AS CONTROLS

Preliminary to the use of Merthiolate in a cream vehicle or base containing triethanolamine and carbitol, fungicidal tests were conducted to determine the individual and combined effect of these chemicals upon such organisms. The optimum concentrations of triethanolamine and carbitol in such a cream base appeared to be about 1:80 and 1:14 respec-

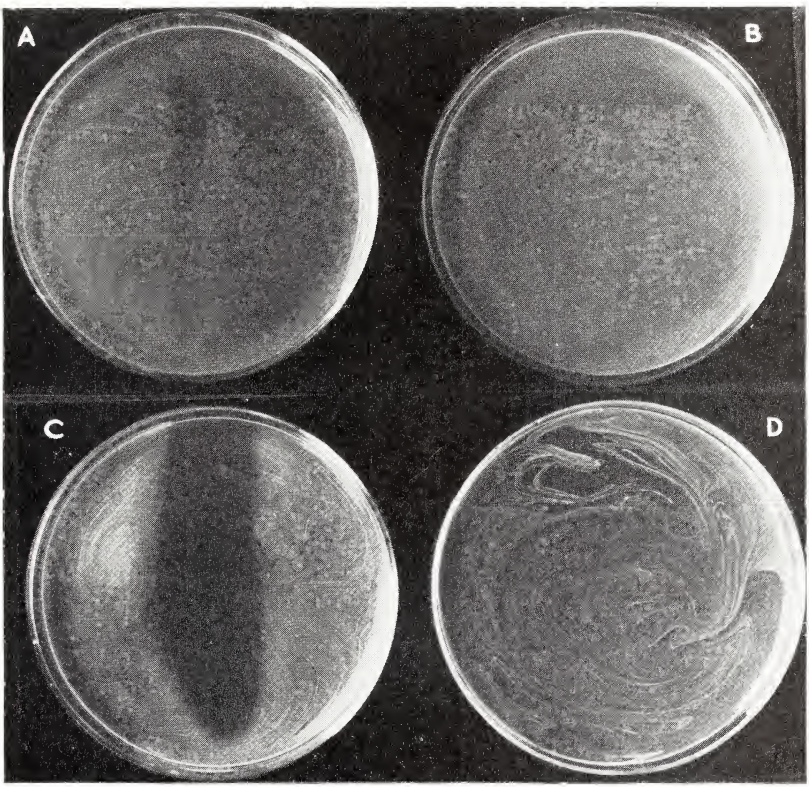

Fig. 6: *Staphylococcus aureus* Poured Agar Plates Prepared by Mixing 0.1 cc. Twenty-Four Hour Broth Culture with 20 cc. Melted Beef Extract Agar, and, After Streaking with a Platinum Loop of the Indicated Materials, Incubating at 37° C. for Twenty-Four Hours.

A. Triethanolamine Undiluted.

B. Carbitol Undiluted.

C. Merthiolate Aqueous Solution 1-1000 Containing Triethanolamine 1-80 and Carbitol 1-14.

D. No Medication.

tively, consequently these concentrations were tested in the combinations with Merthiolate. Table III shows the results of these tests. Both triethanolamine and carbitol when used undiluted proved fungicidal, but when used 1:5 and 1:3 respectively were not fungicidal. Concentrations of these chemicals of 1:80 and 1:14 respectively in a special cream base therefore would appear useful only indirectly as intended, and yet on the other hand not interfere with the fungicidal action of Merthiolate.

TABLE III

Test fungus	Trichophyton purpureum 4183			Epidermophyton rubrum 655		
Exposure of test culture to chemical (minutes)	5	10	15	5	10	15
Triethanolamine:						
Undiluted	—	—	—	—	—	—
1:5	+	+	+	+	+	+
1:10	+	+	+	+	+	+
1:15	+	+	+	+	+	+
1:20	+	+	+	+	+	+
Carbitol:						
Undiluted	—	—	—	—	—	—
1:2	+	+	—	+	—	—
1:3	+	+	+	+	+	+
1:4	+	+	+	+	+	+
1:5	+	+	+	+	+	+
Merthiolate:						
1:1000	—	—	—	—	—	—
2000	—	—	—	—	—	—
3000	—	—	—	—	—	—
4000	—	—	—	—	—	—
5000	—	—	—	—	—	—
Merthiolate (with triethanolamine 1:80)						
1:1000	—	—	—	—	—	—
2000	—	—	—	—	—	—
3000	—	—	—	—	—	—
4000	—	—	—	—	—	—
5000	—	—	—	—	—	—
Merthiolate (with carbitol 1:14)						
1:1000	—	—	—	—	—	—
2000	—	—	—	—	—	—
3000	—	—	—	—	—	—
4000	—	—	—	—	—	—
5000	—	—	—	—	—	—
Merthiolate (with triethanolamine 1:80 and carbitol 1:14)						
1:1000	—	—	—	—	—	—
2000	—	—	—	—	—	—
3000	—	—	—	—	—	—
4000	—	—	—	—	—	—
5000	—	—	—	—	—	—

TABLE IV

Test culture	Staphylococcus aureus 209			
Growth readings after incubation (hours)	24	48	72	168
Merthiolate:				
1:1,000,000	—	—	—	—
2,000,000	—	—	—	—
3,000,000	—	—	—	—
4,000,000	—	—	—	—
5,000,000	—	—	—	—
6,000,000	—	—	—	—
7,000,000	—	—	+	+
8,000,000	—	+	+	+
9,000,000	—	—	+	+
10,000,000	—	—	+	+
Merthiolate (from 1:1000 stock with triethanolamine 1:80)				
1:1,000,000	—	—	—	—
2,000,000	—	—	—	—
3,000,000	—	—	—	—
4,000,000	—	—	—	—
5,000,000	—	—	—	—
6,000,000	—	—	—	—
7,000,000	—	—	—	+
8,000,000	—	—	+	+
9,000,000	—	—	+	+
10,000,000	—	+	+	+
Merthiolate (from 1:1000 stock with carbitol 1:14)				
1:1,000,000	—	—	—	—
2,000,000	—	—	—	—
3,000,000	—	—	—	—
4,000,000	—	—	—	—
5,000,000	—	—	—	—
6,000,000	—	—	—	+
7,000,000	—	—	—	+
8,000,000	—	—	+	+
9,000,000	—	—	+	+
10,000,000	—	—	+	+
Merthiolate (from 1:1000 stock with triethanolamine 1:80 and carbitol 1:14)				
1:1,000,000	—	—	—	—
2,000,000	—	—	—	—
3,000,000	—	—	—	—
4,000,000	—	—	—	—
5,000,000	—	—	—	—
6,000,000	—	—	—	—
7,000,000	—	—	—	+
8,000,000	—	—	+	+
9,000,000	—	—	+	+
10,000,000	—	—	+	+

TABLE V

Test fungus	Staphylococcus aureus 209					
Exposure of test culture to chemical (minutes)	5		10		15	
Culture Series	direct culture	sub-culture	direct culture	sub-culture	direct culture	sub-culture
Phenol:						
1:60	—		—		—	
70	+		+		—	
Triethanolamine:						
Undiluted	+		+		+	
1:5	+		+		+	
10	+		+		+	
15	+		+		+	
20	+		+		+	
Carbitol:						
Undiluted	—	—	—	—	—	—
1:2	+		+		+	
3	+		+		+	
Merthiolate:						
1:1000	—	—	—	—	—	—
2000	—	—	—	—	—	—
3000	—	+	—	—	—	—
4000	+	+	—	—	—	—
5000	+	+	+	+	—	+
Merthiolate (stock 1:1000 with triethanolamine 1:80)						
1:1000	—	—	—	—	—	—
2000	—	—	—	—	—	+
3000	—	+	—	—	—	—
4000	+	+	—	—	—	—
5000	+	+	+	+	—	—
Merthiolate (stock 1:1000 with carbitol 1:14)						
1:1000	—	—	—	—	—	—
2000	—	—	—	—	—	—
3000	—	—	—	—	—	—
4000	—	+	—	—	—	—
5000	+	+	—	+	+	+
Merthiolate (stock 1:1000 with triethanolamine 1:80 and carbitol 1:14)						
1:1000	—	—	—	—	—	—
2000	—	—	—	—	—	—
3000	—	—	—	—	—	—
4000	+	+	+	+	—	—
5000	+	+	+	+	—	+

Antibacterial Tests of Solutions as Controls

For further information as to the desirability of such modifications of Merthiolate *Staphylococcus aureus* inhibition tests were conducted with Merthiolate solution 1:1000 alone and as modified with triethanolamine and carbitol separately and together. The technique of such tests has been described previously[1]. The results of these tests are shown in Table

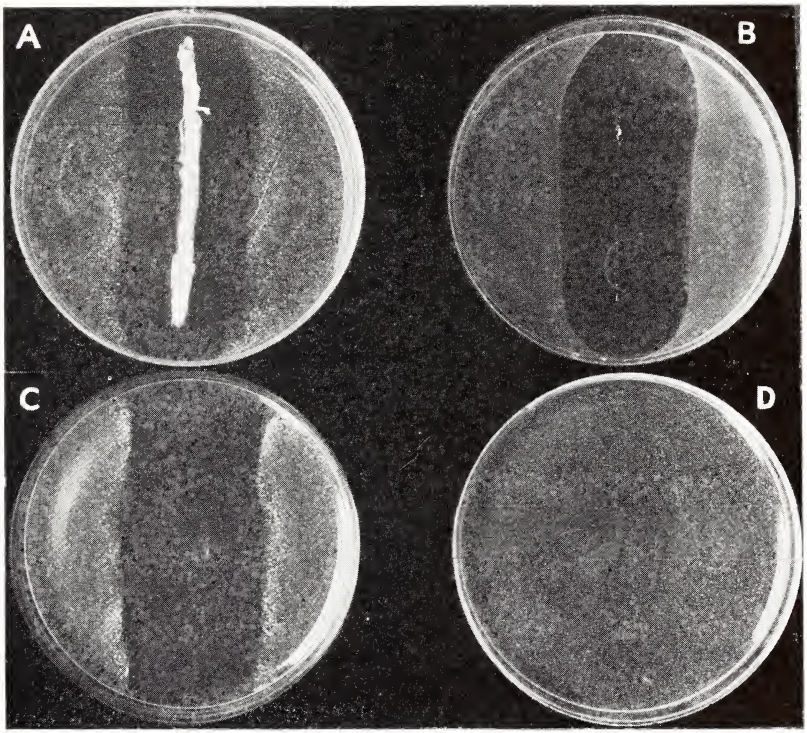

Fig. 7: *Staphylococcus aureus* Poured Agar Plates Prepared by Mixing 0.1 cc. Twenty-Four Hour Broth Culture with 20 cc. Melted Beef Extract Agar, and, After Streaking with a Platinum Loop of the Indicated Materials, Incubating at 37° C. for Twenty-Four Hours.

A. Merthiolate Cream 1-1000, Number 38586-1, Aged Twelve Months at Outside Weather Temperature in Collapsible Tubes.

B. Merthiolate Jelly 1-1000, Number P-25186, Aged Thirteen Months at Room Temperature in Collapsible Tubes.

C. Merthiolate Aqueous Solution 1-1000 as Control.

D. No Medication.

IV, and indicate that triethanolamine and carbitol do not add to or detract from the bacterial inhibitory properties of Merthiolate. The inhibitory properties are somewhat higher as shown here than we previously reported[1].

Germicidal tests were also conducted with Merthiolate, triethanolamine, and carbitol to determine further whether such combination is

desirable. The technique used is essentially that employed in the F. D. A. method[20]. Subcultures were made of culture tubes showing no growth following two days' incubation, and final results were read after seven days' incubation. These results are set forth in Table V, and indicate that carbitol, but not triethanolamine, has a week germicidal action, and that combinations of these with Merthiolate in concentrations mentioned above do not add to or detract from the well known germicidal action of Merthiolate.

FUNGUS PLATE TESTS OF MERTHIOLATE 1:1000 CREAM AND CONTROL MATERIALS

A series of fungus poured plate comparative tests of the general nature previously described[7,16] have been conducted with Merthiolate 1:1000 Cream. The fungi used were *Trichophyton purpureum* 4183 and *Epidermophyton rubrum* 655. The essential procedure utilized consisted in the preparation of glucose agar poured plates, containing fungi throughout the agar, and these were then streaked with a platinum loop of the test chemical. Following incubation of a week, large cleared areas appeared in the plates if the chemical tested possessed fungus inhibitory properties. Subcultures of the agar from such cleared areas have shown that under these conditions Merthiolate is also fungicidal as evidenced by uniform lack of growth in subcultures.

The fungus plates utilized in these tests have been photographed with suitable legends and are shown in Figures 1 to 4. An examination of these plates, including the proper controls, shows that Merthiolate has a readily demonstrable fungus inhibiting property, while triethanolamine has only a very slight action even when used undiluted. Neither carbitol nor the cream base has any demonstrable action on these fungi. It is also apparent that the utilization of triethanolamine and carbitol in the concentrations indicated does not affect either favorably or adversely the pronounced action of Merthiolate on fungi, and that these substances would serve only as indirectly acting materials, as planned, in a cream base with Merthiolate.

BACTERIAL PLATE TESTS OF MERTHIOLATE 1:1000 CREAM AND CONTROL MATERIALS

A further series of poured plates utilizing *Staphylococcus aureus* was prepared as has been described, and when the tests were completed these also were photographed as Figures 5 and 6. These tests show also that one may depend upon a strong antibacterial action of Merthiolate whether it be alone in aqueous solution or in a complex cream base, and also that the ingredients of the latter do not modify such antibacterial action in an appreciable way.

STABILITY OF MERTHIOLATE 1:1000 CREAM

Poured agar plate tests have been conducted as shown in Figure 7 which is nearly self explanatory in light of previous tests. A stability of action of one year is indicated, and deterioration has not been detected in this time.

Discussion

It appears that Merthiolate has fungicidal and fungus inhibiting action sufficient to justify its use in human mycotic skin conditions. We have attempted to improve upon a simple liquid solution for medicating the skin with Merthiolate through use of a semisolid stearate cream prepared by means of triethanolamine and carbitol which latter chemicals appear to have several desirable and unique properties. Both triethanolamine and carbitol in the concentrations suitable for preparation of a Merthiolate Cream base have been shown to have negligible direct action on fungi; however, these accessory materials expedite an emulsification of natural skin oils and thus assure good contact of Merthiolate and the skin.

Conclusions

1. Merthiolate has been shown to have a strong "test-tube" action on fungi associated with human mycotic skin conditions.
2. The action of Merthiolate in a special semisolid cream base on fungi is described from a laboratory point of view.

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INSECT GALLS ON SPECIES OF CUSCUTA

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In a study of the genus Cuscuta carried on now for nearly twenty years, I have had occasion to examine thousands of specimens either in the fresh condition or as herbarium specimens. Different species of these parasitic plants occur in nearly every part of the world and under a great variety of climatic conditions. They occur from Chile to Canada in the Americas, where they are most abundant, and from the Cape of Good Hope to about 60° north latitude in the Old World. Some species parasitize plants with woody stems seemingly as readily as they do those with succulent herbaceous stems, and occasionally they are to be found on the stems of Equisetum or of grasses. Hosts growing under the arid conditions of the desert or in salt marshes apparently serve as well for some Cuscuta species as do those occurring in more favorable growing regions.

One would expect to discover, in the examination of so large a number of specimens gathered from so wide a geographical range and growing under such variable ecological conditions, some specimens which were attacked by plant or animal parasites. In my experience I have seen no specimen which showed positive evidence of fungal parasitism. Saccardo records *Dendryphium macowanianum* as attacking *Cuscuta cassytoides*, and Peck described *Protomyces martindalii* as occurring on *Cuscuta Gronovii* which are the only references I have discovered giving

Cuscuta as a host plant for fungi. In my opinion the species of Cuscuta are free of fungous disease to a remarkable extent.

I have found swollen stems and flower pedicels in a few specimens which were believed to indicate insect gall formation. In most of the specimens seen, however, the material was dry and old and it was not considered worth while attempting to determine the causative insect.

Recently Dr. Chas. C. Deam of the Department of Conservation sent me a specimen of *Cuscuta pentagona* which he had collected a few miles southwest of Lafayette, Indiana, that showed excellent galls. Through the courtesy of Mr. George Burkett of our department I was able to secure from the same station a large quantity of fresh plants bearing numerous galls.

The galls, which occur on the stems and pedicels, are subglobular to oval or somewhat irregular in shape, from 0.3 to 1.0 cm. in length and commonly somewhat longer than thick. The central cavity represents from one-third to one-half of the gall.

Search of the available literature failed to reveal any reference to galls on Cuscuta which would assist in the identification of the causative insect. Specimens were sent to Dr. E. Porter Felt who, in reply, stated "The galls on Cuscuta are with little question those of *Smicronyx sculpticollis* Casey, a small weevel which produces a gall one-eighth to one-fifth of an inch in diameter."

The galls resemble, so far as I can remember, those observed on previous occasions. It is now impossible, of course, to determine if they were produced by *S. sculpticollis* or by some other insect. It is apparent, however, that gall production on Cuscuta is comparatively rare and probably limited to a few insects.

PAPERS FROM THE PROGRAM OF THE CHEMISTRY SECTION

ORGANIC COMPOUNDS OF SELENIUM VI[1]

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SELENONIUM COMPOUNDS

Introduction. In this paper, as in the preceding members of the series, will be found a complete list of the selenonium compounds found in the literature, classified according to their general structure, i.e., $RSeX_3$, R_2SeX_2, etc. The abbreviations used are those commonly used by the American Chemical Society publications. A complete bibliography and a list of the general methods of preparation are tabulated for each compound.

Properties. The following types of selenonium compounds were found in the literature: (1) monoalkyl, (2) monoaryl, (3) dialkyl, (4) diaryl, (5) trialkyl, (6) triaryl, (7) tetra-alkyl, (8) alkyl-aryl, (9) alkyl-hetero, (10) dihetero, (11) di-selenonium, $R = SeX_2SeX_2 — R$, (12) cyclic selenium, and (13) hexavalent (?) selenium.

The selenonium compounds usually contain ionizable inorganic groups. The most outstanding properties are based upon this fact. For example, the inorganic groups are easily replaced by other inorganic groups. Several examples are known in which the selenonium monohydroxide exhibits the properties of a strong base. The trihydroxy selenonium compounds tend to lose water with the resulting formation of a seleninic acid. This may form an addition product with an inorganic acid (either HCl or HNO_3) to give a mixed inorganic radical ($MeSe(OH)_2Cl$).

Selenonium trihydroxides may be reduced by zinc and acid to form selenols. Normally, dihalogen selenonium compounds, when treated with alkalis, form the corresponding dihydroxide or the selenoxide. However, naphthalene derivatives when so treated form selenides.

Diaryl selenonium dihalides are decomposed by heat to form the selenide and a halogenated selenide with the halogen substituted in the ring. This may occur by the two following parallel reactions:

$2\ Ph_2SeBr_2 = Ph_2Se + (C_6H_4Br)_2Se + 2HBr$

$Ph_2SeBr_2 = PhSeC_6H_4Br + HBr.$

Dihydroxyselenonium compounds are easily dehydrated to form the corresponding selenoxide or reduced to the selenide. Trialkyl selenonium halides frequently form crystalline addition compounds with $PtCl_4$ and

[1] This paper is the sixth in a series which will ultimately present a classification of the prepared selenium organic compounds, with a resume of the chemistry and literature pertaining to them.

$ZnCl_2$ $(Me_3SeCl)_2PtCl_4$.). Triaryl selenonium halides are decomposed by heat to form the selenide and an aryl halide.

$Ph_3SeCl = Ph_2Se + PhCl$.

Numerous examples of tetra-alkyl selenonium compounds were reported but no examples were found of tetra-aryl selenonium compounds.

Although a few compounds are reported as possessing hexavalent selenium, the author is inclined to consider them as "poly halides," without assigning the last two valency bonds to the selenium atom. If this assumption is correct, these formulae should be written $R_2SeX_2 \cdot X_2$ instead of R_2SeX_4.

PREPARATION OF SELENONIUM COMPOUNDS

General Methods

Method No.	*Equations*	*Ref. Nos.*
2.	Reported but now considered not to have been prepared.	32, 31, 24, 14, 68, 22, 6½, 72, 61.
3.	Probably prepared but not reported as such in the references.	74½, 61, 13, 14, 53, 72, 21.
4.	All methods not affecting the selenium atom.	45, 11, 53, 49, 54, 5, 19, 35, 30.
5.	$R—SeOOH+HX=RSe(OH)_2X$. (R=Aryl, alkyl; X=Cl,Br,I,NO_3,OH)	80, 2, 71, 74½, 76, 18.
6.	$RSe(OH)_2X+HY=RSeY_3+HX$. (X=NO_3; Y=Br,I. R=Alkyl).	74½.
7.	$RSe—SeR+3X_2=2RX_3$. (X=Br; R=Alkyl).	18.
8.	$R_2Se(OH)X+MY=R_2SeY_2+HX+HOH$. (X=$NO_3$; Y=Cl, I, Br; R=Alkyl, aryl; M=K, H)	31, 32, 33, 71, 15, 37½, 42, 22.
9.	$RSe(OH)_2X+HY=RSeOOH$. HY+HX. (X=Cl, NO_3; Y=Br, I; R=Alkyl)	80, 2.
10.	$R_2Se+O;+HX=R_2Se(OH)X$. (O=HNO_3, $KMnO_4$). (X=NO_3; R=Alkyl.)	31, 32, 22, 37, 45, 81, 39, 25.
11.	$R_2SeX_2+2MY=R_2SeY_2+2MX$. (X=Cl, OH, Br; Y=$SO_4$, Br, Cl, I, OH; M=Na, NH_4, Ag, H, K; R=Alkyl, aryl.)	31, 33, 7, 26, 40, 1, 18.
12.	$RMgX+Se_2X_2=R_2SeX_2+$. .(X=Cl, Br; R=Alkyl)	77.
13.	$RMgX+SeX_4=R_2SeX_2+$. (X=Cl; R=Alkyl)	77.
14.	R_2Se+X_2+(non aq. solvent)$=R_2SeX_2$. (X=Cl, Br, I, OH; R=Alkyl, aryl, hetero).	77, 24, 7, 41, 39, 37, 22, 14, 18, 78, 66, 25, 81, 46, 48, 49, 50, 61.
15.	$R_2Se_2+3X_2+(\text{non aq. solvent})_2=RSeX_2+Se_2X_2$. (R=alkyl; X=Cl, Br.)	77.
16.	$2RSeOOH+PX_5=R_2SeX_2+$. (X=Cl; R=alkyl)	44.
18.	$2R{:}R+2Se_2X_2=(XR—R'—)_2SeX_2+3Se$. (R:R=Ethylenic hydrocarbon; X=Cl)	6, 8½.
19.	$2R{:}R+2SeOX_2=(XR—R—)_2SeX_2+SeO_2$. (X=Cl; R:R′, = ethylenic hydrocarbon.)	23.

20. $R{:}R+2SeX_4=(XR—R—)_2SeX_2+$. 7.
(X=Cl, Br; R:R=ethylenic hydrocarbon)

21. $RNHC(=Se)NH_2+R'X=R'NH(NH_2)C(—Se(X)R)$. 73, 16.
X=I; R=aliphatic; R′=aliphatic.)

22. $2RH+SeX_4=R_2SeX_2+2HX$. 51, 41, 47, 36.
(X=Cl; RH=ketone, alkyl, aryl, hetero)

23. $2RH+SeO_2+2HX=R_2SeX_2+2H_2O$. 41, 1.
(X=Cl; RH=ketone, ether)

24. $2RH+SeOX_2=R_2SeX_2+H_2O+R_3SeX+$. 65, 1, 53.
(X=Cl; RH=ketone, phenol, ether).

26. $R_3SeX+MY=R_3SeY+MX$. 31, 24, 68, 11, 42, 53, 70.
(X=I, NO_3, OH, Br, Cl, O; Y=OH, Cl, I, Br, C_2O_4, NO_3, $HC_4H_4O_6$, $C_6H_2N_2O_7$, d—bromocamphorsulphate, Cr_2O_7, SO_4; M=Ag, H, Et, K, Na; R=alkyl, aryl, d—bromocamphorsulphate).

27. $RX+Se+heat+pressure=R_3SeX+X_2$. 29.
(X=I; R=alkyl)

28. $R_2Se_2+5R'X=RR'_2SeX_3+R'_3SeX+RX$. 10, 31.
(X=I; R′=alkyl; R=alkyl).

29. $RSeSeR+RX=R_2(X)SeSeR$. $R_2(X)SeSeR+MgRX$; $+H_2O=R_3SeSeH+MgX_2+ROH$. 67.
(R=alkyl; X=Br).

30. $2R_2SeX_2+ZnR_2=2R_3SeX\cdot ZnX_2$. 71.
(R=alkyl·X=Cl).

31. $R_2Se+R'X=R'R_2SeX$. 69, 68, 11, 70, 18.
(R=alkyl, aryl. X=I, Br).

32. $R_2SeX+RH+AlCl_3=R_3SeX+HCl$. 42.
(R=aryl; X=Cl).

33. $SeX_4+RH+AlCl_3=R_2Se_2+R_2Se+R_3SeX+$. 14, 13, $12\frac{3}{4}$.
(R=aryl; X=Cl).

34. $SeO_2+RH+AlX_3=R_3SeX$. (X=Cl; R=ether). 29, $28\frac{1}{2}$.

35. $SeO_2+RNH_2+HX=R_3SeX+$. 20.
(R=aryl. X=SO_4H).

36. $Se+RNH_2+HX=R_3SeX+$. (R=aryl; X=SO_4H). 20.

37. $2R'SeH+H_2RX_2=R'_2Se=R+2HX+H_2Se+$. 24.
(R=alkyl; R′=aklyl; X=Br.)

Method No.	*Equations*	*Ref. Nos.*
38.	$OR—Se=Se—RO + \text{Heat (or catalyst)} = R'_2 \equiv Se +$. (R = Acylalkyl; R′ = acylalkyl).	60.
40.	$2R(NH_2)_2 + H_2SeO_3 = (R(NH—)_2 \equiv Se$.	30, 72.
41.	$RR'R''SeX + X_2 = RR'SeX_2 + R''X$. (R = aryl; R′ = carboxyalkyl; R″ = alkyl; X = Br).	18.
42.	$2R_2SeX_2 + MOH = R(X)Se—O—Se(X)—R +$. (M = NH_4; X = Cl; R = Alkyl).	68.
43.	$R_2Se_2 + 2X_2 = RSeX_2—SeX_2R$. (R = aryl, alkyl, hetero; X = Br, Cl, I).	77, 24, 52.
44.	$SeX_4 + RM = OR—Se=Se—RO + RX + MX +$. (R = acylalkyl; X = Cl; M = H, Cu).	58, 59, 60, 63, 62.
45.	$OR—Se=Se—RO + 2HX = HORSe \equiv SeROH + X2$. (R = acylalkyl; X = I).	60, 63, 62.
46.	$4SeX_4 + 5RM = 2R—Se \equiv Se—R + 6RX + 5MX_2$. (R = acylketone; X = Cl; M = Cu).	60.
47.	$OR—Se—Se—RO$ (Se) $+ 2HX = HORSe \equiv SeROH + Se + X_2$. (R = acylalkyl; X = I).	60.
48.	$\left.\begin{matrix} R=SeX_2 \\ \text{or} \\ R \equiv SeX \end{matrix}\right\} + MY = R=SeY_2 + MX$. (R = Se = heterocyclic Se cmpd.) ($X_2 = I_2$, Br_2Cl_2, HNO_3, SO_4H, OH; Y = OH, NO_3; M = Ag, Na, H).	56, 54, 55, 19, 27, 5, 17½.

49. $R=Se+X_2=R=SeX_2$. (R=Se=Heterocyclic compd; $X_2=HNO_3I_2$, Cl_2, Br_4, alkyl halide). 56, 49, 24, 54, 57, 27, 35, 57, 55, 17½.

50. $R=SeX_2+R=SeY_2=2RSeXY$. (R=hetero). 54.

51. $R_2Se+heat=OR-\overline{Se=Se}-OR+$. (R=acylalkyl). 60.

52. $R=SeO+HX=R=Se(OH)X$. ($X=NO_3$, OH; R=Se=heterocyclic Se compd.) 27, 17½.

53. $RNO+H_2Se;+FeCl_3+HCl=N=R_2=SeCl$. (R=hetero). 17.

54. $SeX_4+3MR=\overline{OR-Se-Se-Se-RO}+4RX+3MX_2+2HX$. 60.

(R=acylalkyl; M=Cu; X=Cl).

LIST OF SELENONIUM COMPOUNDS

	Names (*Se≡*) = *Selenonium*)	*Formulas*	*M. P. or B. P.°C.*	*Methods of Prep.*	*Ref. Nos.*
		MONO-ALKYL-			
1.	Methyl-Se≡dihydroxy chloride	$MeSe(OH)_2Cl$	M=88-90.	5	80,
2.	Methyl-Se≡dihydroxy bromide	$MeSe(OH)_2Br$	D=————	9	80,
3.	Methyl-Se≡dihydroxy iodide	$MeSe(OH)_2I$	————	9	80,
4.	Ethyl-Se≡dihydroxy chloride	$EtSe(OH)_2Cl$	M=106	9, 5	74½, 2, 71
5.	Ethyl-Se≡dihydroxy nitrate	$EtSe(OH)_2NO_3$	M=73	5,	2,
6.	Ethyl-Se≡tridromide	$EtSeBr_3$	D=73	6.	74½,
7.	Ethyl-Se≡triiodide	$EtSeI_3$	————	3.	74½
		MONO-ARYL-			
1.	Phenyl-Se≡Dihydroxy nitrate	$PhSe(OH)_2NO_3$	M=112	5	76, 38,
2.	Phenyl-Se≡trihydroxide	$PhSe(OH)_3$	M=122-4	5,	76,
3.	*p*-Tolyl-Se≡tribromide	p:$MeC_6H_4SeBr_3$	M=113-4	5, 7, 3,	18, 61
4.	*p*-Bromophenyl-Se≡tribromide	p:$BrC_6H_3SeBr_3$	D=————	3,	61, 18,
		DI-ALKYL-			
1.	Dimethyl=Se=dichloride	Me_2SeCl_2	M=59.5	8,	31, 32,
2.	Dimethyl=Se=dibromide	Me_2SeBr_2	D=82=M	8,	31, 32,
3.	Dimethyl=Se=diiodide	Me_2SeI_2	D=————	8,	31, 32,
4.	Dimethyl=Se=hydroxynitrate	$Me_2Se(OH)NO_3$	M=90.5		
			S=<100	10,	31, 32,
5.	Dimethyl=Se=sulfate	Me_2SeSO_4	————	11,	31,
6.	Dibenzyl=Se=dichloride	$(PhCH_2)_2SeCl_2$	M=128	2, 12, 13,	32, 31, 24,
			=134.5	14, 8?	77, 44,
7.	Dibenzyl=Se=dibromide	$(PhCH_2)_2SeBr_2$	M=84?	14?, 2, 12,	77, 32, 24
			=105.5	15, 32?	
8.	Dibenzyl=Se=diiodide	$(PhCH_2)_2SeI_2$	M=97.	14?, 2,	24, 31,
9.	Dibenzyl=Se=hydroxynitrate	$(PhCH_2)_2Se(OH)NO_3$	M=88	10?, 2,	32, 31, 24,
10.	Diethyl=Se=dichloride	Et_2SeCl_2	M=————	8,	33, 71,
11.	Diethyl=Se=hydroxychloride	$Et_2Se(OH)Cl$	M=————	3, 11,	33.
12.	Diethyl=Se=dibromide	Et_2SeBr_2	————	8,	33,
13.	Diethyl=Se=hydroxybromide	$Et_2Se(OH)Br$	————	11,	33,

14.	Diethyl=Se=diiodide	Et_2SeI_2	B=————	11,	33,
15.	Diethyl=Se=hydroxyiodide	$Et_2Se(OH)I$	————	11,	33,
16.	Diethyl=Se=hydroxynitrate	$Et_2Se(OH)NO_3$	————	10,	33
17.	Di(*B*-chlorethyl)=Se=dichloride	$(ClCH_2CH_2)_2SeCl_2$	M=121.5 =122.5	18, 19, 20,	6, 23, 8½ 8, 7
18.	Di(*B*-chlorethyl)=Se=dibromide	$(ClCH_2CH_2)_2SeBr_2$	M=D=117	11,	7,
19.	Di(*B*-Bromethyl)=Se=dichloride	$(BrCH_2CH_2)_2SeCl_2$	M=98-9	14,	7,
20.	Di(*B*-Bromethyl)=Se=dibromide	$(BrCH_2CH_2)_2SeBr_2$	M=118	20,	7,
21.	Compd. of ethyl iodide+ allylselenocarbamide	$EtNHC(NH_2)=Se(C_3H_5)I$	M=100	21,	73,
22.	Di(Benzoylmethylene)=Se=dichloride	$(BzCH_2)_2SeCl_2$	M=121.5 =122	22, 23, 24,	51, 41, 65, 47
23.	Di(Benzoylmethylene)=Se=dibromide	$(BzCH_2)_2SeBr_2$	M=102	14,	41,
24.	Di(Benzoylmethylene)=Se=diiodide	$(BzCH_2)_2SeI_2$	M=112	————	41,
25.	Di(*p*-chlorobenzoyl-methylene)= Se=dichloride	$(p\text{:}ClBzCH_2)_2SeCl_2$	M=126	24,	65,
26.	Di(*p*-anisoylmethylene)=Se=dichloride	$(p\text{:}MeOC_6H_4COCH_2)_2SeCl_2$	M=122	22,	41,
27.	Di(*p*-toluylmethylene)=Se=dichloride	$(p\text{:}MeC_6H_4COCH_2)_2SeCl_2$	M=129 =132	22, 24,	41, 65
28.	Di(*p*-toluylmethylene)=Se=dibromide	$(p\text{:}MeC_6H_4COCH_2)_2SeBr_2$	M=112	14,	41,
29.	Di(*x*-cumuylmethylene)=Se=dichloride	$(x\text{:}Me_2CHC_6H_4COCH_2)_2SeCl_2$	M=119	22,	41,
30.	Di(*2-4*-xyloylmethylene)=Se=dichloride	$(2,4\text{:}Me_2C_6H_3COCH_2)_2SeCl_2$	M=128	22,	41,
31.	Di(*2*-Me-*5*-Isopr-benzoyl-methylene=Se=dichloride	$(2\text{:Me-}5\text{:}iso\text{pr}C_6H_3COCH_2)_2SeCl_2$	M=133	24,	65,
32.	(*2-4-6*-ψ-cumuylmethylene) =Se=dichloride	$(2,4,6\text{:}Me_3C_6H_2COCH_2)_2SeCl_2$	M=139	22,	41,
33.	Di(*p*-phenyl-benzoylene-methylene=Se=dichloride	$(p\text{:}PhC_6H_4COCH_2)_2SeCl_2$	M=136	22,	41,
34.	Di(*x*-naphthoylmethylene)= Se=dichloride	$(x\text{:}C_{10}H_7COCH_2)_2SeCl_2$	M=116	————	41,
35.	Di(*p*-acetylphenylene-carbamylmethylene=Se=dichloride	$(p\text{:}AcC_6H_4NHCOCH_2)_2SeCl_2$	M=130	22,	41,
36.	Di(*B*-chloropropyl)=Se=dichloride	$(CH_3CHClCH_2)_2SeCl_2$	M=80, 81	19, 18, 20,	23, 8½, 7,
37.	Di(Acetylmethylene)=Se=dichloride	$(CH_3COCH_2)_2SeCl_2$	M=81, 82	22, 24,	51, 65
38.	Di(Benzoylethylene)=Se=dichloride	$(BzCH_2CH_2)_2SeCl_2$	M=118, 124	22, 24,	41, 65
39.	Di(*x*-naphthoylethylene=Se=dichloride	$(x\text{:}C_{10}H_7COCH_2CH_2)_2SeCl_2$	M=————	22,	41,

LIST OF SELENONIUM COMPOUNDS—Continued

	Names (*Se*≡) = *Selenonium*)	*Formulas*	*M. P. or B. P.°C.*	*Methods of Prep.*	*Ref. Nos.*
40.	Di(*B*-chlorobutyl=Se=dichloride	$(CH_3CH_2CHClCH_2)_2SeCl_2$	B=————	18, 19,	8½, 23,
41.	Di(*B*-chloramyl)=Se=dichloride	$(CH_3CH_2CH_2CHClCH_2)_2SeCl_2$	B=85-100	18, 19,	23, 8½,
		DI-ARYL-			
1.	Diphenyl=Se=dihydroxide	$(Ph_2Se(OH)_2$	————	2,	14, 42, 12½,
2.	Diphenyl=Se=dichloride	Ph_2SeCl_2	M=182, 142, 183-3, 5, 181-2, 179-80,	2, 14, 8, 3, 10,	46, 37, 45, 22, 37½, 39, 42, 14
3.	Diphenyl=Se=dichloride diacetone	$Ph_2SeCl_2+2CH_3COCH_3$	M=127.8-7.9	4,	45,
4.	Diphenyl=Se=dibromide	Ph_2SeBr_2	M=140, 141, 148, 154, 141-2, 112?	14, 3,	46, 77, 18, 78, 39, 37½, 66, 37, 13, 14, 12, 7½, 65½
5.	Diphenyl=Se=hydroxynitrate	$Ph_2Se(OH)NO_3$	M=97	10,	22,
6.	Di(3-hydrobromoaminoPh)= Se=dibromide	$(3{:}HBrH_2NC_6H_4)_2SeBr_2$	M=115-6	14,	66,
7.	4-Acetaminodiphenyl=Se= dihydroxide	$4{:}AcHNC_6H_4(Ph)=Se=(OH)_2$	M=147-8	14,	26,
8.	4-Acetaminodiphenyl=Se=dichloride	$4{:}AcHNC_6H_4(Ph)=Se=Cl_2$	M=131-2	10,	26,
9.	4-Acetaminodiphenyl=Se=dibromide	$4{:}AcHNC_6H_4(Ph)=Se=Br_2$	M=135-6	14,	26,
10.	4-Acetaminodiphenyl=Se=diiodide	$4{:}AcHNC_6H_4(Ph)=SeI_2$	M=144-5	14, 11, 10,	26,
11.	Di(4-anisyl)=Se=dihydroxide	$(4{:}MeOC_6H_4)_2Se(OH)_2$	M=134, 137	11,	1, 40,
12.	Di(4-anisyl)=Se=dichloride	$(4{:}MeOC_6H_4)_2SeCl_2$	M=163	10,	1, 40,
13.	Di(4-anisyl)=Se=dibromide	$(4{:}MeOC_6H_4)_2SeBr_2$	M=124, 125	14,	1, 40,
14.	Di(4-anisyl)=Se=diiodide	$(4{:}MeOC_6H_4)_2SeI_2$	M=————	14,	40,
15.	Di(3-Br-4-anisyl)=Se=dihydroxide	$(3{:}Br{:}4{:}MeOC_6H_3)_2Se(OH)_2$	M=150	11,	1,
16.	Di(3-Br-4-anisyl)=Se=dichloride	$(3{:}Br{:}4{:}MeOC_6H_4)_2SeCl_2$	M=180	24,	1,
17.	Di(3-Br-4-anisyl)=Se=dibromide	$(3{:}Br{:}4{:}MeOC_6H_4)_2SeBr_2$	M=87	14,	1,
18.	Di(3-Me-4-anisyl)=Se=dihydroxide	$(3{:}Me{:}4{:}MeOC_6H_4)_2Se(OH)_2$	M=91	11,	1,
19.	Di(3-Me-4-anisyl)=Se=dichloride	$(3{:}Me{:}4{:}MeOC_6H_4)_2SeCl_2$	M=155-8	24,	1,
20.	Di(3-Me-4-anisyl)=Se=dibromide	$(3{:}Me{:}4{:}MeOC_6H_4)_2SeBr_2$	M=136	14,	1,
21.	Di(4-phenetyl)=Se=dihydroxide	$(4{:}EtOC_6H_4)_2Se(OH)_2$	M=145, 146-8	11,	1, 40

22.	Di(*4*-phenetyl)=Se=dichloride	$(4{:}EtOC_6H_4)_2SeCl_2$	M=139, 140	24,	1, 40
23.	Di(*4*-phenetyl)=Se=dibromide	$(4\text{-}EtOC_6H_4)_2SeBr_2$	M=117, 123,	14,	1, 40
24.	Di(*4*-phenetyl)=Se=diiodide	$(4{:}EtOC_6H_4)_2SeI_2$	M=96,	14, 11,	40,
25.	Di(*4*-propoxyphenyl)=Se=dihydroxide	$(4{:}PrOC_6H_4)_2Se(OH)_2$	M=51-4	11,	1,
26.	Di(*4*-propoxyphenyl)=Se=dichloride	$(4{:}PrOC_6H_4)_2SeCl_2$	M=91,	24,	1,
27.	Di(*4*-propoxyphenyl)=Se=dibromide	$(4{:}PrOC_6H_4)_2SeBr_2$	M=69,	14,	1,
28.	Di(*4*-butoxyphenyl)=Se=dihydroxide	$(4{:}BuOC_6H_4)_2Se(OH)_2$	M=58-60,	11,	1,
29.	Di(*4*-butoxyphenyl)=Se=dichloride	$(4{:}BuOC_6H_4)_2SeCl_2$	M=93,	24,	1,
30.	Di(*4*-butoxyphenyl)=Se=dibromide	$(4{:}BuOC_6H_4)_2SeBr_2$	M=65,	14,	1,
31.	Di(*4*-phenoxyphenyl)=Se=dihydroxide	$(4{:}PhOC_6H_4)_2Se(OH)_2$	M=122-5,	11,	1,
32.	Di(*4*-phenoxyphenyl)=Se=dichloride	$(4{:}PhOC_6H_4)_2SeCl_2$	M=135-40,	24,	1
33.	Di(*4*-phenoxyphenyl)=Se=dibromide	$(4{:}PhOC_6H_4)_2SeBr_2$	M=113,	14,	1.
34.	Ph-4-Tolyl=Se=dibromide	$4{:}CH_3C_6H_4(Ph)SeBr_2$	M=149-50,	14,	25,
35.	Di(*2*-Tolyl)=Se=dichloride	$(2{:}CH_3C_6H_4)_2SeCl_2$	M=152-3,	10,	46, 81,
36.	Di(*2*-Tolyl)=Se=dibromide	$(2{:}CH_3C_6H_4)_2SeBr_2$	M=84	14,	46, 81,
37.	Di(*4*-Tolyl)=Se=dichloride	$(4{:}CH_3C_6H_4)_2SeCl_2$	M=177-8 177.5-8.5	8,	46, 15, 81,
38.	Di(*4*-Tolyl)=Se=dibromide	$(4{:}CH_3C_6H_4)_2SeBr_2$	M=162	14,	46, 81,
39.	Di(*p*-cresyl-*3*-)=Se=dichloride	$(1{:}Me{:}4{:}OH{:}C_6H_3{:}3\text{-})_2SeCl_2$	———	———	53,
40.	Di(*2*-carboxyphenyl)=Se=dihydroxide	$(2{:}HOOCC_6H_4)_2Se(OH)_2$	———	———	43,
41.	*4*-carboxydiphenyl=Se=dibromide	$4{:}HOOCC_6H_4(Ph)SeBr_2$	M=205-7, 208-10	10, 14,	25,
42.	Di(*alpha*-naphthyl)=Se=dichloride	$(\alpha{:}C_{10}H_7)_2SeCl_2$	M=130,	14,	46,
43.	Di(*alpha*-naphthyl)=Se=dibromide	$(\alpha{:}C_{10}H_7)_2SeBr_2$	M=183,	14,	46,
44.	Di(*beta*-naphthyl)=Se=dichloride	$(B{:}C_{10}H_7)_2SeCl_2$	M=146,	14,	46,
45.	Di(*beta*-naphthyl)=Se=dibromide	$(B{:}C_{10}H_7)_2SeBr_2$	M=161,	14,	46, 37,

TRI-ALKYL-

1.	Trimethyl≡Se-hydroxide	Me_3SeOH	———	26,	31,
2.	Trimethyl≡Se-chloride	Me_3SeCl	———	26,	31, 30½,
3.	Trimethyl≡Se-iodide	Me_3SeI	———	27, 28,	29, 10, 31, 74,
4.	Dimethylbenzyl≡Se-hydroxide	$Me_2(C_7H_7)SeOH$	———	26,	31
5.	Dimethylbenzyl≡Se-iodide	$Me_2(C_7H_7)SeI$	———	28,	29,
5½.	Dibenzylmethyl≡Se-iodide	$Me(C_7H_7)_2SeI$	———	———	30½.
6.	Tribenzyl≡Se-chloride	$(C_6H_5CH_2)_3SeCl$	M=92	26, 3,	24, 31,
7.	Tribenzyl≡Se-bromide	$(C_6H_5CH_2)_3SeBr$	———	26, 3,	31, 24,
8.	Tribenzyl≡Se-iodide	$(C_6H_5CH_2)_3SeI$	———	26, 3,	31, 24,

LIST OF SELENONIUM COMPOUNDS—Continued

	Names (*Se*≡) = *Selenonium*)	*Formulas*	*M. P. or B. P.°C.*	*Methods of Prep.*	*Ref. Nos.*
9.	Tribenzyl≡Se-nitrate	$(C_6H_5CH_2)_3SeNO_3$	M=88, 102-3	3,	32, 31, 24.
10.	Triethyl≡Se-hydroxide	Et_3SeOH	———	26,	68, 69,
11.	Triethyl≡Se-hydroselenide	Et_3SeSeH	———	29,	67,
12.	Triethyl≡Se-chloride	Et_3SeCl	———	26, 30,	71, 68,
13.	Triethyl≡Se-bromide	Et_3SeBr	———	2,	6½,
14.	Triethyl≡Se-iodide	Et_3SeI	D=80-126	28, 31,	29, 10, 69, 68, 69, 74,
15.	Triethyl≡Se-acid oxalate	$Et_3SeC_2O_4H$	———	26,	68, 69,
16.	Triethyl≡Se-acid tratrate	$Et_3SeC_4H_4O_6H+2H_2O$	———	26,	68, 69,
17.	Methyldiethyl≡Se-bromide	$Et_2(Me)SeBr$	———	4,	11,
18.	Carboxymethyldiethyl≡Se-hydroxide	$Et_2(HOOCCH_2)SeOH$	———	26,	11,
19.	Carboxymethyldiethyl≡Se-chloride	$Et_2(HOOCCH_2)SeCl$	———	26,	11,
20.	Carboxymethyldiethyl≡SeBr	$Et_2(HOOCCH_2)SeBr$	M=74	31	11,
21.	Addn. compd. of allylseleno-carbamide and EtI	$CH_2=CHCH_2NH(NH_2)=Se(Et)I$	M=100	21	16, 73,
22.	Addn. compd. of ethylseleno-carbamide and allylbromide	$EtNH(NH_2)=Se(CH_2=CHCH_2)Br$	M=115	21	73.
		TRI-ARYL-			
1.	Triphenyl≡Se-hydroxide	Ph_3SeOH	———	———	42,
2.	Triphenyl≡Se-chloride	Ph_3SeCl	D=230	32, 33, 3,	42, 9, 14, 13, 12¼, 14¾,
3.	Triphenyl≡Se-bromide	Ph_3SeBr	D=236	26,	42,
4.	Triphenyl≡Se-iodide	Ph_3SeI	D=237.5	26,	42,
5.	Triphenyl≡Se-nitrate	Ph_3SeNO_3	M=107-8	26,	42,
6.	Triphenyl≡Se-picrate	$Ph_3SeC_6H_2(NO_2)_3O$	M=141-2	26,	42,
7.	Triphenyl≡Se-dichromate	$(Ph_3Se)_2Cr_2O_7$	D=238	26	42
8.	Tri-*2*?-hydroxyphenyl≡Se-oxide	$((2?:HOC_6H_4)_3Se)_2O$	———	26	53
9.	Tri-*2*?-hydroxyphenyl≡Se-chloride	$(2?:HOC_6H_4)_3SeCl$	D=125	3, 24,	53
10.	Tri-*4*-hydroxyphenyl≡Se-oxide	$((4:HOC_6H_4)_3Se)_2O$	D=240	26,	53
11.	Tri-*4*-hydroxyphenyl≡Se-chloride	$(4:HOC_6H_4)_3SeCl$	M=232	24,	53
12.	Tri-*4*-hydroxyphenyl≡Se-bromide	$(4:HOC_6H_4)_3SeBr$	D=237	26	53
13.	Tri-*4*-hydroxyphenyl≡Se-nitrate	$(4:HOC_6H_4)_3SeNO_3$	———	26,	53,

14.	Tri-*4*-hydroxyphenyl〓Se-sulfate	$((4{:}HOC_6H_4)_3Se)_2SO_4$	D = 269-70	26,	53,
15.	Tri-*3*-bromo-*4*-hydroxyphenyl 〓Se-oxide	$((3{:}Br;4{:}HOC_6H_3)_3Se)_2O$	M = 198	26,	53,
16.	Tri-*3*-bromo-*4*-hydroxyphenyl 〓Se-bromide	$(3{:}Br{:}4;HOC_6H_3)_3SeBr$	M = 251	26,	53,
17.	Tri-*3*-*5*-dibromo-*4*-hydroxyphenyl 〓Se-bromide	$(3{:}5{:}Br_2{:}4{:}HOC_6H_2)_3SeBr$	D = 261	4,	53,
18.	Tri-*p*-cresyl-*3*〓Se-oxide	$((1{:}Me{:}4{:}HOC_6H_3{:}3\text{-})_3Se)_2O$	D = 160	26,	53,
19.	Tri-*p*-cresyl-*3*〓Se-chloride	$(1{:}Me{:}4{:}HOC_6H_3{:}3\text{-})_3SeCl$	D = 260-5	24,	53,
20.	Tri-*5*-bromo-*p*-cresyl-*3*〓Se-bromide	$(1{:}Me{:}5{:}Br{:}4{:}HOC_6H_2{:}3\text{-})_3SeBr$	D = 195	———	53,
21.	Tri-*o*-cresyl-*3*〓Se-oxide	$((1{:}Me{:}2{:}HOC_6H_3{:}3\text{-})_3Se)_2O$	D = 236	26,	53,
22.	Tri-*o*-cresyl-*3*〓Se-chloride	$(1{:}Me{:}2{:}HOC_6H_3{:}3\text{-})_3SeCl$	D = 231	24	53
23.	Tri-*o*-cresyl-*3*〓Se-nitrate	$(1{:}Me{:}2HOC_6H_3{:}3\text{-})_3SeNO_3$	D = 224	26,	53,
24.	Tri-*5*-bromo-*o*-cresyl-*?*〓Se-bromide	$(1{:}Me{:}5{:}Br{:}2{:}HOC_6H_2{:}?\text{-})_3SeBr$	D = 253	26,	53,
25.	Tri-*2*-*4*-dihydroxyphenyl〓Se-chloride	$(2{:}4{:}(HO)_2C_6H_3)_3SeCl$	M = 206	24	53
26.	Tri-*2*?-anisyl〓Se-chloride	$(2?{:}MeOC_6H_4)_3SeCl$	M = 54-5	———	53,
27.	Tri-*4*-anisyl〓Se-hydroxide	$(4{:}MeOC_6H_4)_3SeOH$	B = ———	26	29, 28½, 53.
28.	Tri-*4*-anisyl〓Se-chloride	$(4{:}MeOC_6H_4)SeCl$	B = ———	34, 4,	29, 28½, 56
29.	Tri-*4*-anisyl〓Se-iodide	$(4{:}MeOC\ H\ )\ SeI$	B = ———	26,	29, 28½, 53,
30.	Tri-*4*-anisyl〓Se-dichromate	$((4{:}MeOC_6H_4)_3Se)_2Cr_2O_7$	M = 68-70	26,	29, 28½, 53
31.	Tri-*m*-dimethoxyphenyl-*x*- =Se-chloride	$(m{:}(MeO)_2C_6H_3{:}x\text{-})_3SeCl$	———	34,	29,
32.	Tri-*4*-phenetyl〓Se-hydroxide	$(4{:}EtOC_6H_4)_3SeOH$	———	26,	29, 28½
33.	Tri-*4*-phenetyl〓Se-chloride	$(4{:}EtOC_6H_4)\ SeCl$	———	34,	29, 28½, 53,
34.	Tri-*4*-phenetyl〓Se-iodide	$(4{:}EtOC_6H_4)_3SeI$	B = ———	26,	28½,
35.	Tri-*p*-acetaminophenetyl-*x*〓 Se-acid sulfate	$(p\text{-}AcNH(EtO)C_6H_3)_3SeSO_4H+HOH$	M = 260	35, 36,	20,
		TETRA-ALKYL-			
1.	Dibenzyl = Se = ethylene	$(PhCH_2)_2Se = (\text{-}CH{=}CH\text{-})$	M = 68-9	37,	24,
2.	Bis dibenzoylmethane〓Se	$(Bz_2CH_2{=})_2Se$	M = 190-1	38,	60,
3.	Di(*1*-*8*-naphthylene-*sec*-diamine〓Se	$(C_{10}H_6{:}1{:}8(NH)_2{=})_2Se$	M = 120	40, 3,	30, 72,
4.	*1*-*8*-naphtho-*2'*-*6'*-selendi-azine	$C_{10}H_6{:}1{:}8{:}(N)_2〓Se$	———	2,	72, 30
		TETRA-ARYL-			
	None	None	———	———	———

LIST OF SELENONIUM COMPOUNDS—Continued

ALKYL-ARYL-

	Names (*Se*☰) = *Selenonium*)	*Formulas*	*M. P. or B. P.°C.*	*Methods of Prep.*	*Ref. Nos.*
1.	Phenylmethyl=Se=dihydroxide	$Ph(Me)Se(OH)_2$	B=————	11,	18,
2.	Phenylmethyl=Se=dichloride	$Ph(Me)SeCl_2$	M=122	8, 10,	22,
3.	Phenylmethyl=Se=dibromide	$Ph(Me)SeBr_2$	M=115-6	14,	18,
4.	Phenylmethyl=Se=bromiodide	Ph(Me)SeBrI	M=85	11,	18,
5.	Phenylmethyl=Se=diiodide	$Ph(Me)SeI_2$	M=69-71	11,	18,
6.	Phenylmethyl=Se=hydroxynitrate	$Ph(Me)Se(HO)NO_3$	M=97	10,	22,
7.	Phenylethyl=Se=dichloride	$Ph(Et)SeCl_2$	M=64-5	10, 8,	22,
8.	Phenylethyl=Se=dibromide	$Ph(Et)SeBr_2$	M=84	14,	18,
9.	Phenylethyl=Se=hydroxynitrate	$Ph(Et)Se(HO)NO_3$	B=————	10,	22,
10.	Phenyl (carboxymethylene) =Se=dibromide	$Ph(HOOCCH_2)SeBr_2$	M=126	14,	18,
11.	*4*-Bromophenyl (carboxymethylene) =Se=dibromide	$4{:}BrC_6H_4(HOOCCH_2)SeBr_2$	D=120-30	14,	61,
12.	*4*-Carboxyphenyl (carboxymethylene) =Se=dibromide	$4{:}HOOCC_6H_4(HOOCCH_2)SeBr_2$	M=198-9	14,	25,
13.	*4*-Tolyl (carboxymethylene)= Se=dibromide	$4{:}MeC_6H_4(HOOCCH_2)SeBr_2$	M=100-1, 103-4, D=90-100.	14, 41	18, 61,
14.	Phenyl *iso*-amyl=Se=dichloride	$Ph(Me_2CHCH_2CH_2)SeCl_2$	M=80	8, 10	22,
15.	Phenyl *iso*-amyl=Se=hydroxynitrate	$Ph(Me_2CHCH_2CH_2)Se(OH)NO_3$	B=————	10,	22,
16.	Phenylmethylcarboxy-methylene ☰Se-Cl	$Ph(Me)(HOOCCH_2)SeCl$	————	26,	70
17.	Phenylmethylcarboxy-methylene☰ Se-bromide	$Ph(Me)(HOOCCH_2)SeBr$	M=111, 110-1	31,	70, 18
18.	Phenylmethylcarboxy-methylene☰ Se-iodide	$Ph(Me)(HOOCCH_2)SeI$	————	26,	70,
19.	*4*-Tolylmethylcarboxy-methylene☰ Se-bromide	$4{\text-}MeC_6H_4(Me)(HOOCCH_2)SeBr$	M=100	31,	18,
20.	*d*-Phenylmethylcarboxy-methylene☰ Se-*d*-bromo-camphorsulfonic acid	$Ph(Me)(HOOCCH_2)SeC_9H_{13}O(Br)SO_3H$	M=168	26,	70,
21.	*L*-Phenylmethylcarboxy-methylene☰ Se-*d*-bromo-camphorsulfonic acid	$Ph(Me)(HOOCCH_2)SeC_9H_{13}O(Br)SO_3H$	M=157	26,	70,

ALKYL-HETERO-

1. Methyl-(1-phenyl-3-methyl-pyrro(*a*) monazolyl-5-)=Se=dichloride	Me(NPh-N=CMe-CH=C-)$SeCl_2$	M=128	14,	48,
2. Methyl-(*1*-phenyl-*3*-methyl-pyrro(*a*) monazolyl-*5*-)=Se=dibromide	Me(NPh-N=CMe-CH=C-)$SeBr_2$	M=110	14,	48,
3. Methyl-(*x*-dibromo-*1*-phenyl-*3*-methyl-pyrro(*a*)monazolyl-*5*-)=Se=dibromide	Me(NPh-N=CMe-CH=C-)$SeBr_2+Br_2$	M=191	14, 3,	50,
4. Methyl-(*1*-methyl-*3*-phenyl-pyrro(*a*) monazolyl-*5*-)=Se=dichloride	Me(NMe-N=CPh-CH=C-)$SeCl_2$	M=161	14,	49,
5. Methyl-(*1*-Methyl-*3*-phenyl-pyrro(a) monazolyl-*5*-)=Se=dibromide	Me(NMe-N=CPh-CH=C-)$SeBr_2$	M=177	14,	49,

DI HETERO-

1. Di(*1*-phenyl-*2*-*3*-dimethyl-pyrro(*a*) monazolonyl-*4*-)=Se=dichloride	(CMe-NMe=NPh-CO-C-)$_2SeCl_2$	M=225	22,	36

DISELENONIUM

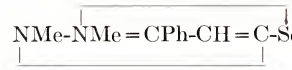
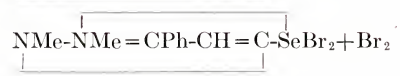
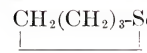
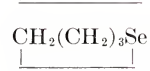
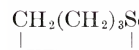
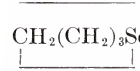
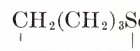
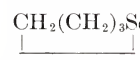
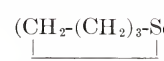
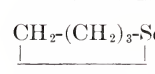
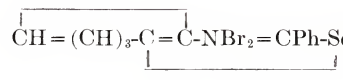
1. Diethyl diselenonium* oxydichloride *Abbreviated as $\equiv Se_2\equiv$ or $=Se\equiv$	Et_2=Se-O-Se=Et_2	———	42, 2,	68,
2. Diphenyl=$Se_2\equiv$tetrabromide	$PhSeBr_2SeBr_2Ph$	M=111	43,	77,
3. Dibenzyl=$Se_2\equiv$tetrabromide	$PhCH_2SeBr_2SeBr_2CH_2Ph$	M=134, 137,	43,	77, 24,
4. Dibenzyl=$Se_2\equiv$tetraiodide	$PhCH_2SeI_2SeI_2CH_2Ph$	M=98	43,	24,
5. Di(*1*-Phenyl-*3*-methyl-*4*-benzoyl-*5*-) $=Se_2\equiv$tetrachloride	(NPh-N=CMe-CBz=C-$SeCl_2$-)$_2$	M=125	43,	52,
6. Di(*1*-phenyl-*3*-methyl-*4*-Benzoyl-*5*-) $=Se_2\equiv$tetrabromide	(NPh-N=CMe-CBz=C-$SeBr_2$-)$_2$	M=201	43,	52,
7. Di(*1*-phenyl-*3*-methyl-*4*-Benzoyl-*5*-) $=Se_2\equiv$tetraiodide	(NPh-N=CMe-CBz=C-SeI_2-)$_2$	M=78	43,	52,

LIST OF SELENONIUM COMPOUNDS—Continued

	Names (*Se☰*) = *Selenonium*)	*Formulas*	*M. P. or B. P.°C.*	*Methods of Prep.*	*Ref. Nos.*
8.	"Dimeric selenium acetylacetone"	$(CAc=CMe\text{-}O\text{-}Se=Se\text{-}O\text{-}CMe=CAc$	M = 175, 185	44,	58, 59,
		or**			64, 60, 63,
	**In order to save space this and similar compounds will be represented as:	$(CAc=CMe\text{-}O\text{-}Se=)_2$.			
9.	"Diselenium bisacetylacetone"	$(HOCMe=C(Ac)\text{-}Se☰)_2$	———	45,	60,
10.	"Diselenium bis-*C*-ethyl-acetylacetone"	$(EtC(Ac)_2Se☰)_2$	M = 117-8	46,	60,
11.	"Diselenium bisacetyl-propionylmethane"	$(CH_3CH_2COH=CAc\text{-}Se☰)_2$	———	45,	63,
12.	"Diselenium bisbenzoylacetone"	$(MeC(OH)Bz\text{-}Se☰)_2$	M = 80-90	45, 47,	60,
13.	"Diselenium bisdibenzoyl-methane"	$(PhCOH=CBz\text{-}Se☰)_2$	M = 116-8	45,	60,
14.	"Diselenium bis-*w*-phenyl-acetylacetone"	$(MeCOH=C(COCH_2Ph)\text{-}Se☰)_2$ or $(PhCH_2COH=CAc\text{-}Se☰)_2$	———	45,	62,
15.	"Diselenium bis-*B*-phenyl-propionylacetone"	$(MeCOH=C(COCH_2CH_2Ph)\text{-}Se☰)_2$ or $(PhCH_2CH_2COH=CAc\text{-}Se☰)_2$	———	45,	62,
16.	"Compound"	$Ph_3Se_2C_6H_4Cl$	B_{100} = 245-50	33	12¾

SELENONIUM COMPOUNDS CONTAINING CYCLIC SELENIUM.

1.	Cyclo=Se=propane-*1-1*-dihydroxide	$CH_2CH_2CH_2Se(OH)_2$	———	48,	56,
2.	Cyclo=Se=propane-*1-1*-diiodide	$CH_2CH_2CH_2SeI_2$	M = 98	49,	56,
.	*1-2*-Dimethyl-*3*-phenyl pyrro(*a*) monazolyl-*2-5*=Se=dichloride	$NMe\text{-}NMe=CPh\text{-}CH=C\text{-}SeCl_2$	M = 163	49,	49.

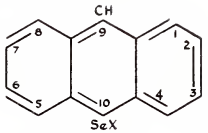
4.	*1-2*-Dimethyl-*3*-phenyl pyrro(*a*) monazolyl-*2-5*=Se=dibromide		M=215	4,	49,
5.	*x-x*-Dibromo-*1-2*-dimethyl-*3*-phenyl-pyrro(*a*)monazolyl-*2-5*=Se=dibromide		M=108	49,	49,
6.	Cyclo=Se=butane-*1-1*-dihydroxide		————	48,	54,
7.	Cyclo=Se=butane-*1*-hydroxy-*1*-chloride		D=116	48,	54,
8.	Cyclo=Se=butane-*1-1*-dichloride		M=88-9	49,	54,
9.	Cyclo=Se=butane-*1*-hydroxy-*1*-bromide		D=99-100	48, 50,	54,
10.	Cyclo=Se=butane-*1-1*-dibromide		M=92	49, 3,	54, 21,
11.	Cyclo=Se=butane-per-bromide		D————	4, —	54,
12.	Cyclo=Se=butane-*1-1*-diiodide		M=99-100	49,	54,
13.	Cyclo=Se=butane-*1-1*-methiodide		M=174	————	54,
14.	*Alpha-delta*-(*1-1'*-bis-cyclo=Se=butane-*1-1'*-dibromide)tetramethyene		M=95-6	49,	54,
15.	*Alpha*-Bromo-*delta*-(*1*-cyclo=Se=butane-*1*-bromide)		M=65-6	49,	54,
16.	*1-3*-Tetrabromo-*2*-phenyl-*4-5*-benzoselen-(b)-monazole		M=134	49,	24,

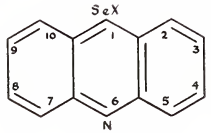
LIST OF SELENONIUM COMPOUNDS—Continued

	Names (*Se*☰) = *Selenonium*)	*Formulas*	*M. P. or B. P.°C.*	*Methods of Prep.*	*Ref. Nos.*
17.	*1-3*-Tetraiodo-*2*-phenyl-*4-5*-benzoselen(b)monazole	$CH=(CH)_3\text{-}C=C\text{-}NI_2=CPh\text{-}SeI_2$	M=84	49,	24,
18.	"Selenium acetylpropionyl-methane"	$(CAc=CEt\text{-}O\text{-}Se=)_2$**			
		or $(C(EtCO)=CMe\text{-}O\text{-}Se=)_2$**	M=137	44,	63,
19.	"Dimeric selenium benzoyl acetone"	$(CBz=CMe\text{-}O\text{-}Se=)_2$**	M=212	44,	60, 58,
20.	"Dimeric selenium-*omega*-phenyl acetyl acetone"	$(CAc=C(C_7H_7)\text{-}O\text{-}Se=)_2$**			
		or $(C(PhCH_2CO)=CMe\text{-}O\text{-}Se=)_2$**	M=164-5	44,	62,
21.	"Dimeric selenium-*beta*-phenyl propionyl acetone"	$CAc=C((CH_2)_2Ph)\text{-}O\text{-}Se=)_2$**			
		or $(C(OC(CH_2)_2Ph)=CMe\text{-}O\text{-}Se=)_2$**	M=141-2	44,	62,
22.	"Selenium dibenzoylmethane"	$(CBz=CPh\text{-}O\text{-}Se=)_2$**	M=211	44,	60

23.	"Isoseleniumbenzoylmethane"	$CBz=CPh\text{-}O\text{-}Se=Se\text{-}CBz=CPh\text{-}O$	M=175-6	51,	60,
24.	Cyclo=Se=pentane-*1-1*-dihydroxide	$CH_2(CH_2)_4Se(OH)_2$	————	48,	55,
25.	Cyclo=Se=pentane-*1*-hydroxy-*1*-chloride	$CH_2(CH_2)_4Se(OH)Cl$	D=110-11	48,	55,
26.	Cyclo=Se=pentane-*1-1*-dichloride	$CH_2(CH_2)_4SeCl_2$	M=103	49,	55,
27.	Cyclo=Se=pentane-*1-1*-dibromide	$CH_2(CH_2)_4SeBr_2$	M=117-8	49,	55,
28.	Cyclo=Se=pentane-perbromide	$CH_2(CH_2)_4SeBr_2+5Br$	D————	49,	55,
29.	Cyclo=Se=pentane-*1-1*-diiodide	$CH_2(CH_2)_4SeI_2$	M=114	49,	55,
30.	Cyclo=Se=pentane-*1-1*-methiodide	$CH_2(CH_2)_4Se(Me)I$	M=165-6	49,	55,
31.	*Alpha*-Bromo-*beta*-(*1*-cyclo=Se=pentane-*1*-bromide) dimethylene	$CH_2(CH_2)_4Se(Br)CH_2CH_2Br$	M=88	49,	55,
32.	*2*-Methylcyclo=Se=pentane-*1-1*-dichloride	$MeCH(CH_2)_4SeCl_2$	B=————	49,	57,
33.	*2*-Methylcyclo=Se=pentane-*1-1*-dibromide	$MeCH(CH_2)_4SeBr_2$	————	49,	57,
34.	*2*-Methylcyclo=Se=pentane-*1-1*-diiodide	$MeCH(CH_2)_4SeI_2$	————	49,	57,
35.	*2*-Methylcyclo=Se=pentane-*1-1*-methiodide	$MeCH(CH_2)_4Se(Me)I.$	M=164	49,	57,

LIST OF SELENONIUM COMPOUNDS—Continued

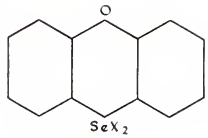
	Names (*Se*☰) = *Selenonium*)	Formulas	M. P. or B. P. °C.	Methods of Prep.	Ref. Nos.
36.	*3-6*-Diaminoselenxanthene-*10*-chloride	*3:6*:$(NH_2)_2C_{13}H_7SeCl$***	———	48,	19,
	***$C_{13}H_9SeX$ = selen xanthene-*10*-halide				
37.	*3-6*-Tetramethyldiaminoselenxanthene-*10*-chloride	*3:6*:$(Me_2N)_2C_{13}H_7SeCl$	———	———	4,
38.	*3-6*-Tetramethyldiamino-*9*-cyanoxanthene-*10*-nitrate	*3:6*:$(Me_2N)_2$:*9*:$CNC_{13}H_6SeNO_3$	———	49,	3,
39.	*3-6*-Bisdiazoselenzanthene-*10*-hydroxide	*3:6*:$(HONN)_2C_{13}H_7SeOH$	———	48,	19,
40.	*3-6*-Bisdiazoselenzanthene-*10*-chloride	*3:6*:$(CINN)_2C_{13}H_7SeCl$	———	4,	19,
41.	*3*-Dimethylamino-*6*-ethylamino-selenxanthene-*10*-chloride	*3*:(Me_2N):*6*:$(EtHN)C_{13}H_7SeCl$	———	———	4,
42.	*2-7*-Dimethyl-*3-6*-diamino-selenxanthene-*10*-acid sulfate	*2:7*:Me_2:*3:6*$(H_2N)_2C_{13}H_5SeSO_4H$	———	———	4,
43.	*2-7*-Dimethyl-*3-6*-diethylamino-selenxanthene-*10*-chloride	*2:7*:Me_2:*3:6*:$(EtHN)_2C_{13}H_5SeCl$	———	———	4,
44.	*2-7*-Dichlor-*3-6*-diamino-selenxanthene-*10*-acid sulfate	*2:7*:Cl_2:*3:6*:$(H_2N)_2C_{13}H_5SeSO_4H$	———	———	4,
45.	*2-7*-Dimenthoxy-*3-6*-diamino selenxanthene-*10*-acid sulfate	*2:7*:$(MeO)_2$:*3:6*:$(H_2N)_2C_{13}H_5SeSO_4H$	———	———	4,
46.	*1-4-5-8*-Tetramethyl-*2-7*-diaminoselenxanthene-*10*-acid sulfate	*1:4:5:8*:Me_4:*3:6*$(H_2N)_2C_{13}H_3SeSO_4H$	———	———	4,
47.	*1-4*-Selenoxan dichloride	$CH_2CH_2OCH_2CH_2SeCl_2$	M = 127-9	49,	27,
48.	*1-4*-Selenoxan dibromide	$CH_2CH_2OCH_2CH_2SeBr_2$	M = 152	49, 48,	27,
49.	*1-4*-Selenoxan diiodide	$CH_2CH_2OCH_2CH_2SeI_2$	M = 106-7	49,	27,

50.	*1-4*-Selenoxan hydroxynitrate	$CH_2CH_2OCH_2CH_2Se(OH)NO_3$	D=140-1	52,	27,
51.	*1-4*-Selenoxan methiodide	$CH_2CH_2OCH_2CH_2Se(Me)I$	M=171	49,	27,
52.	Cyclotetramethylene=Se_2≡ tetrabromide	$CH_2(CH_2)_3SeBr_2SeBr_2$	————	49,	54,
53.	*3*-Phenylaminophenselenazine-*1*-chloride	**** *3*:$PhHNC_{12}H_7SeCl$	————	35,	4,
	****Phenselenazine halide=	$C_{12}H_8NSeX$ or 			
54.	Phenselenazine-*1*-tribromide	$C_{12}H_8NSeBr+Br_2$	————	49,	35,
55.	*3*-(Phenylamino)phenselenazine-*1-3'*-arsonic acid	*3*:(*3*^{1}:AsO_3H:C_6H_4HN)$C_{12}H_7NSe$	————	4,	35,
56.	*3*-(*6'*-Hydroxyphenylamino)-phenselenazine-*1-3'*-arsonic acid	*3*:(*3'*:AsO_3H(*6'*:OH)C_6H_3HN)$C_{12}H_7NSe$	————	4,	35,
57.	*3-5*-Diaminophenselenazine-*1*-hydroxide	*3:5*:$(NH_2)_2C_{12}H_6NSeOH$	————	48,	5,
58.	*3-5*-Diaminophenselenazine-*1*-chloride	*3:5*:$(NH_2)_2C_{12}H_6NSeCl+3H_2O$	————	4,	5, 35,
59.	*3-5*-Diaminophenselenzaine-*1*-nitrate	*3:5*:$(NH_2)_2C_{12}H_6NSeNO_3$	————	48,	5,
60.	*3-5*-Diaminophenselenazine-*1*-dichromate	(*3:5*:$(NH_2)_2C_{12}H_6NSe)_2Cr_2O_7$	————	48,	5,
61.	*3-5*-Diacetylaminoselenazine-*1*-chloride	*3:5*:$(AcHN)_2C_{12}H_6NSeCl$	————	4,	35,
62.	*3-5*-Diacetylamino-*9*-phenyl-aminophenselenazine-*1*-chloride	*3:5*:$(AcHN)_2$:*9*:$(PhHN)C_{12}H_5NSeCl$	————	4,	35,
63.	*3-9*-Diaminophenselenazine-*1*-chloride	*3:9*:$(H_2N)_2C_{12}H_6NSeCl$	————	4,	35, 17,
64.	*3-9*-Dimethylaminoselenazine-*1*-chloride (Selenomethylene Blue)	*3:9*:$(Me_2N)_2C_{12}H_6NSeCl$	————	53,	17, 79, 34, 35,

LIST OF SELENONIUM COMPOUNDS—Continued

	Names (*Se*≡) = *Selenonium*)	*Formulas*	*M. P. or B. P.°C.*	*Methods of Prep.*	*Ref. Nos.*
65.	*3:9*:Dimethylaminephenselenazine-*1*-bromide	*3:9*:$(Me_2N)_2C_{12}H_6NSeBr$	————	4,	35,
66.	*3-5-9*-Triaminophenselenazine-*1*-hydroxide	*3:5:9*:$(H_2N)_3C_{12}H_5NSeOH$	————	48,	5,
67.	*3-5-9*-Triaminophenselenazine-*1*-chloride	*3:5:9*:$(H_2N)_3C_{12}H_5NSeCl+1\frac{1}{2}H_2O$	————	4,	5,
68.	*3-5-9*-Triaminophenselenazine-*1*-nitrate	*3:5:9*:$(H_2N)_3C_{12}H_5NSeNO_3$	————	48,	5,
69.	*3-5-9*-Triaminophenselenazine-*1*-dichromate	$(3:5:9:(H_2N)_3C_{12}H_5NSe)_2Cr_2O_7$	————	48,	5,
70.	"Cyclotriseleniumbisbenzoylacetone"	BzC=CMe-O-Se-Se-Se-O-CMe=CBz	M=190-200	54,	60,
71.	Cyclo=Se=hexane-*1-1*-dichloride	$CH_2(CH_2)_5SeCl_2$	M=78	49,	57,
72.	Cyclo=Se=hexane-*1-1*-dibromide	$CH_2(CH_2)_5SeBr_2$	M=118-9	49,	57,
73.	Dicylo=Se=hexane-*1-1*-dibromide	$(CH_2(CH_2)_5SeBr-)_2$	M=145	49,	57,
74.	Polycyclo=Se=hexane-*1-1*-dibromide	$(CH_2(CH_2)_5SeBr_2)X$	M=94-5	49,	57,
75.	Cyclo=Se=hexane-*1-1*-diiodide	$(CH_2(CH_2)_5SeI_2$	M=82	49,	57,
76.	Cyclo=Se=hexane-*1-1*-methiodide	$(CH_2(CH_2)_5Se(Me)I$	D=149-50.	49,	57,
77.	Cyclopentamethylene-*1-2*=Se_2≡ tetrabromide	$CH_2(CH_2)_4SeBr_2SeBr_2$	————	49,	55,

78.	Cyclohexamethylene-*1-5*=Se_2= tetrachloride	$(CH_2)_3SeCl_2(CH_2)_3SeCl_2$	———	48,	56,
79.	Cyclohexamethyene-*1-5*=Se_2= tetraiodide	$(CH_2)_3SeI_2(CH_2)_3SeI_2$	D=100	48	56,
80.	Cyclohexamethylene-*1-5*=Se_2= tatranitrate	$(CH_2)_3Se(NO_3)_2(CH_2)_3Se(NO_3)_2$	D=87	49,	56,
81.	Phenoxselenine‡ dihydroxide	$C_{12}H_8OSe(OH)_2$	———	52,	17½

‡Phenoxselenine dihalide =  or $C_{12}H_8OSeX_2$

82.	Phenoxselenine dichloride	$C_{12}H_8OSeCl_2$	———	49,	17½
83.	Phenoxselenine dibromide	$C_{12}H_8OSeBr_2$	———	49,	17½
84.	Phenoxselenine di acid sulfate	$C_{12}H_8OSe(HSO_4)_2$	———	48,	17½

HEXAVALENT SELENIUM

1.	*4*-Bromophenyl (carboxymethylene) selenonium tetrabromide	$4{:}BrC_6H_4(HOOCCH_2)SeBr_2+Br_2$	D=———	14, 2,	61, 18,
2.	*4*-Tolyl (carboxymethylene) selenonium tetrabromide	$4{:}CH_3C_6H_4(HOOCCH_2)SeBr_2+Br_2$	D=———	2,	61, 18,
3.	Di-*peri*-naphthaselen-diazole″	$1{:}NHC_{10}H_6{:}8{:}N=Se=1{:}NC_{10}H_6{:}8{:}NH$	M>300	4,	30.

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THE ADSORPTIVE CAPACITY OF SILICAS FOR BENZENE VAPOR

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Research in the preparation of activated silicic acid gel has been in two fields: first, in the reagents used for the preparation of the gel, and second, in the physical or mechanical features of its preparation. Activated silicic acid gels have been prepared from the following reagents: sodium silicate and hydrochloric acid (1), nitric acid (2), sulfuric acid (3), carbon dioxide (4), sulfur dioxide (4), chlorine (5), ferric chloride (6), copper sulfate (6, 7, 8), aluminum chloride (6), aluminum sulfate (6), chromium sulfate (6), and also by hydrolysis of silicon halides or sulfide (9, 10).

Holmes and his associates (6, 7) found that when a gel was placed in a stoppered bottle it tended to exude water, and that such a gel upon being washed free from impurities, dried and activated possessed a higher adsorptive capacity than gels not similarly treated; and, that the adsorptive capacity of a gel could be increased by boiling with 6N to 9N sulfuric acid (the so-called "wet heat treatment gel"). It was also pointed out by Holmes that the presence of tri-valent ferric ions had a strong precipitating effect upon the colloidal silicic acid always present in a solution of sodium silicate.

Holmes and his associates also found that if calcium chloride, cupric chloride, chromium chloride, or aluminum chloride were used in place of ferric chloride in the preparation of silicic acid gel the results were less satisfactory. The explanation given was that there is an optimum sized capillary for each gas or vapor and that the gels produced by use of calcium chloride, etc., did not approach the optimum. According to Bancroft (11) the state of subdivision and the proper regulation of the pectizing agent could also aid in accounting for this.

Recently I. G. Farben Industrie, Ger. 530,730, prepared an activated gel from water glass and gaseous carbon dioxide and sulfur dioxide. This method is unique in that the sodium silicate and silicic acid mixture undergoes gentle constant stirring as the gas bubbles through.

M. O. Kharmandaryan and S. L. Kappellevich (12) have prepared activated silica gel from sodium silicate using hydrochloric acid, sulfuric acid, ferric chloride, and aluminum chloride. They found that a slight excess of acid above the neutralization point greatly reduced the adsorbing power of the gel for benzene vapor. The speed of introduction of acid and cessation of stirring after gelation do not affect the activity of the gel. The gel obtained by precipitation with the minimum quantity of acid produced the lowest yield of gel possessing the maximum activity.

The object of this investigation was to compare the adsorptive capacities of various activated silicas for benzene vapor.

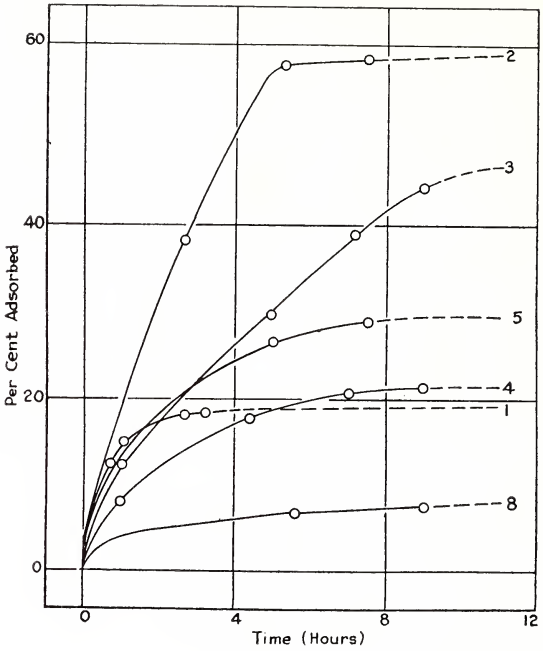
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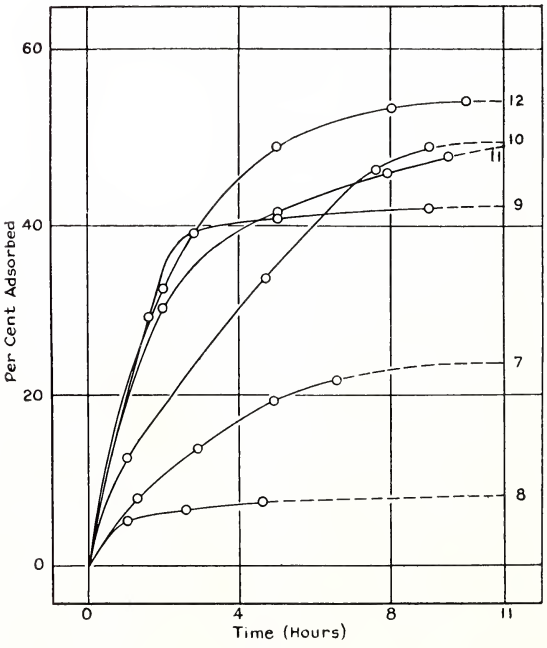
Fig. 1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Per Cent Adsorbed
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7
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Fig. 2

EXPERIMENTAL

Materials: The sodium silicate, commercial quality, sp. gr. 1.38, was obtained from Mallinckrodt Chemical Company. The ferric chloride, copper sulfate and aluminum sulfate were of C. P. quality from J. T. Baker Company. A sample of silica gel (Table 1, gel 24) was obtained from the Silica Gel Corporation of Baltimore, Maryland (Grade ½, No. 150-G-600-1420).

Preparation of Gels: The activated silica gels were prepared according to the methods outlined in Table 1. The gels were precipitated from solutions of sodium silicate of the indicated sp. gr. by the addition of the particular precipitating agent. The stirring method and time of stirring is indicated in the table. After precipitation the gels were filtered and washed in a Buchner funnel on a cloth or paper filter. The gels were then spread out on a cloth supported by ¼-inch mesh galvanized screen for a definite period of time. Some gels were allowed to sweat by placing in a closed glass vessel at room temperature for a period of days. Other gels were placed directly in an oven at 100° C. for drying. After drying, gels numbers 1-19 inclusive were activated for four hours at 450° C. while numbers 20-23 inclusive were activated four hours at 250° C. After activation, the gels were allowed to stand over night in a desiccator. The following day their adsorptive capacities for benzene vapor were determined by passing a stream of air saturated with benzene vapor at 25° C. over a weighed portion of the gel according to the method outlined by Holmes (13).

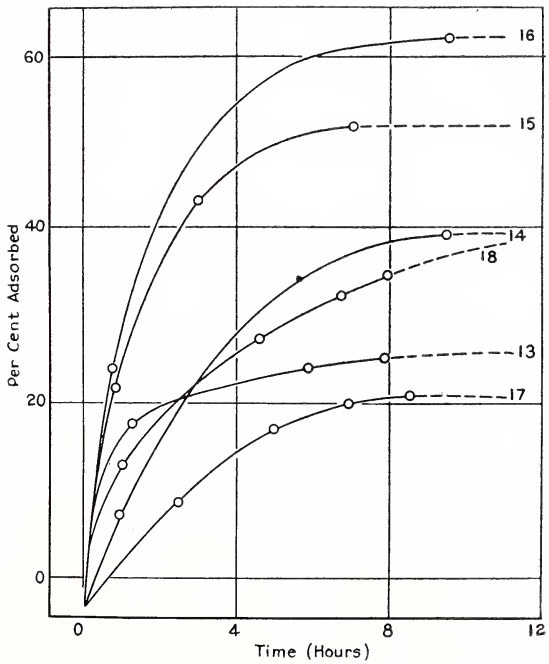

Fig. 3

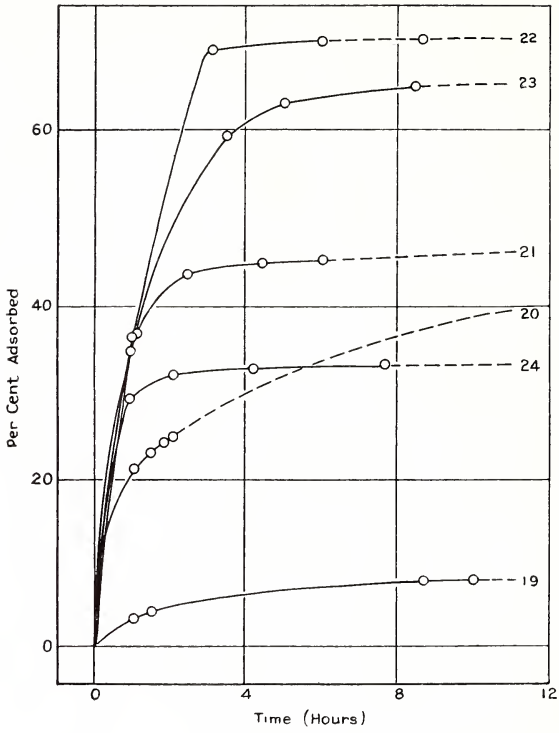

Fig. 4

Gel 1 was stirred by means of bubbling carbon dioxide for ten minutes at fifteen-minute intervals until gelation started, and then was allowed to stand until complete gelation occurred. Gel 2 was stirred in the same manner as 1 except that the stirring was continued beyond the point of gelation as long as mechanically possible. Gel 8 was stirred mechanically for thirty seconds at intervals of three minutes.

Gel 20 was prepared in the same manner as Holmes' wet heat treatment gel up to the point where it was to be given the wet heat treatment, at which time it was washed with hot water until free of chlorides. The ferric oxide was removed by washing with 5 per cent hot sulfuric acid solution and then with hot water until free from sulphates. Gel 21 was given the Holmes wet heat treatment (13).

In the preparation of certain gels pectizing agents were added: gel 22, 100 cc. of 30 per cent ferric chloride solution, and gel. 23, 100 cc. of 30 per cent copper sulfate solution. In preparing these gels the amount of pectizing agent was regulated by first adding a given amount of acid and then adding slowly with constant shaking the given amount of pectizing agent whereupon precipitation occurred.

Data: The last column of Table 1 shows the per cent of benzene vapor adsorbed by the various silica gels. Figs. 1-4 inclusive show the curves obtained when the per cent of benzene vapor adsorbed is plotted

against the time in hours that the gels were exposed to the air saturated with benzene vapor (25° C.). From these curves a comparison of the rates of adsorption can be made.

TABLE 1

No. of Gel.	Sp. gr. Na_2SiO_3 Sol.	Gms. of Na_2SiO_3 Sol.	Ppting. Agent[1]	Stirring Method	Minutes Stirred[2]	Cc. of Ppting. Agt. Added	Filter Used	Time on Screen in Days	Sweating Days	Hrs. Dried 100° Oven	Per Cent Benzene Vapor Absorbed
1	1.06	970.8	CO_2	CO_2 gas	42	.....	cloth	2.58	2.5	48	18.22
2	1.06	1078.0	SO_2	SO_2 gas	17	.....	cloth	2.58	2.6	48	58.27
3	1.06	1657.0	HNO_3	air	52	40.2	cloth	2.0	2.08	48	43.49
4	1.06	1176.0	HNO_3	air	49	28.4	cloth	2.0	2.08	48	22.50
5	1.06	1060.0	HNO_3	air	20	28.4	cloth	2.0	.....	24	29.26
6	1.06	1060.0	HNO_3	.....	.....	28.4	cloth	2.0	.....	24	8.96
7	1.06	1060.0	HNO_3	mech	30	28.4	cloth	2.0	2.05	36	21.24
8	1.06	1060.0	HNO_3	mech	30	28.4	cloth	2.0	2.5	36	7.77
9	1.06	1060.0	H_2SO_3	.....	.....	29.0	paper	2.0	2.0	24	77.8
10	1.06	1060.0	H_2SO_3	.....	.....	29.0	paper	2.0	.....	24	47.76
11	1.06	1060.0	H_2SO_4	mech	20	29.0	paper	2.0	.....	24	42.72
12	1.06	1088.5	HCl	air	17	18.4	cloth	2.0	2.08	48	54.39
13	1.06	1285.7	HCl	.....	.....	21.6	cloth	2.0	2.08	48	25.11
14	1.06	1060.0	HCl	air	25	45.6	paper	1.0	2.0	24	39.53
15	1.06	1060.0	HCl	air	25	45.6	paper	1.0	2.0[3]	24	52.04
16	1.06	1060.0	HCl	air	25	45.6	paper	1.0	2.0[4]	24	62.75
17	1.06	1060.0	HCl	mech	20	45.6	paper	1.0	.....	24	20.89
18	1.06	1060.0	HCl	mech	20	45.6	paper	1.0	2.0	24	35.74
19	1.06	1060.0	H_2SO_3	mech	35	29.0	paper	1.0	.....	24	8.65
20	1.019	1274.0	$FeCl_3$	shaken	2	4000[5]	paper	7.0	7.0	48	27.84
21[6]	1.019	1274.0	$FeCl_3$	shaken	2	4000[5]	paper	7.0	7.0	36	50.45
22	1.016	5080.0	HCl	shaken	2	15.0	paper	4.0	6.0	36	74.05
23	1.016	5080.0	H_2SO_3	shaken	2	15.0	paper	3.0	6.0	36	66.55
24	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	31.55

[1] The acids used were concentrated and of C.P. quality. The sulfuric acid was prepared by adding 356 cc. of conc. H_2SO_4 to 1000 cc. H_2O.

[2] When stirring was accomplished by bubbling of gas or air, the rate of gas flow was held at 7 liters per hour.

[3] Gel number 15 was sweat under a pressure of 15 pounds per sq. in. The pressure was obtained from compressed carbon dioxide.

[4] Gel number 16 was sweat at 50° C.

[5] The ferric chloride solution was 2N.

[6] Gels numbers 21-23 inclusive were given the wet heat treatment.

RESULTS

A comparison of gels 1 and 2, Table 1, shows that a gel prepared from sulfur dioxide and sodium silicate has an adsorptive capacity greater than one made from carbon dioxide and sodium silicate. Gel 2, however, was stirred beyond the point at which gelation occurred, which may account for some of this difference.

In general, the use of paper as a filter was superior to the use of cloth, which is probably due to the fact that more colloidal silicic acid is retained.

The use of nitric acid as precipitating agent produced gels of lower adsorptive capacity for benzene vapor than either sulfuric or hydrochloric acid.

A comparison of gel 9 with 10 and 17 with 18 shows that sweating is important in increasing the adsorptive capacity of gels from benzene vapor.

Gel 5, which was prepared in a manner analogous to 6, except that during the addition of nitric acid it was stirred by means of a current

of air bubbling through the solution, had a much higher adsorptive capacity than gel 6. This indicates that air stirring is an important factor in increasing the adsorptive capacity of these silica gels for benzene vapor. Mechanical stirring seems to cause a slight decrease in the adsorptive capacity if gel 11 is compared with gel 10. Intermittent mechanical stirring (gel 8) is a disadvantage over continuous stirring (gel 7) in the production of a highly active gel.

A comparison of gels 14, 15 and 16 shows that it is advantageous to sweat gels at a pressure of 15 pounds per sq. in. and also to sweat the gels at an elevated temperature (50° C.). It was noted that as soon as gel 15 was subjected to a pressure of 15 pounds per sq. in. at room temperature it began to sweat, which seemed to indicate that sweating was due to vapor pressure within the containing vessel. Gel 16 was sweat at 50° C. in a closed vessel at atmospheric pressure and gel 14 was sweat at room temperature in a closed vessel at atmospheric pressure. It can be concluded that sweating at an elevated temperature, consequently higher vapor pressure, is more desirable than sweating at room temperature.

A possible explanation of the increased adsorptive capacity due to sweating is that increased pressure causes increased coagulation of the colloidal silicic acid, thus preventing its loss during washing. The growth of new filaments between the older and larger filaments will increase the amount of surface exposed and thus increase the adsorptive capacity of the gel.

According to Bancroft (11) a plane surface will adsorb a certain amount of gas under standard conditions, but two plane surfaces placed close together will apparently adsorb more gas than the same surfaces would if each did not reinforce the other and modify the concentration gradient. Perhaps the fact that the adsorptive capacity of a gel increases when it is sweat or subjected to pressure is due to the forcing of the filaments closer together by vapor pressure or applied pressure. This seems to confirm in part Holmes' (14) statement, "Surely there must be a rearrangement of gel particles during this ageing to yield the firmest gel structure."

A comparison of gels 12 and 14 indicates that the addition of an excessive amount of hydrochloric acid (gel 14) decreases the adsorptive capacity. This supports the claim of M. O. Kharmandaryan and S. L. Kappellevich (12) that a slight excess of acid above the neutralization point reduces the activity of the gel.

A comparison of gel 20 with 21 shows the advantage of the wet heat treatment.

A better adjustment of the pectizing agent appears to aid in the preparation of a more active gel. This can be seen from a comparison of gel 21 with 22. To the latter was added hydrochloric acid in addition to the ferric chloride in order to modify the action of the pectizing agent.

Methods of preparation of activated silicas outlined above result in the production of many gels more highly active for the adsorption of benzene vapor than the sample of silica (gel 24) obtained from the Silica Gel Corporation.

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CATALYTIC OXIDATION OF THE CARBOHYDRATES AND RELATED COMPOUNDS BY OXYGEN IN THE PRESENCE OF IRON PYROPHOSPHATES

III. Ethyl Alcohol, Acetaldehyde, Acetic Acid, and Sodium Acetate

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Since ethyl alcohol, acetaldehyde, and acetic acid all represent products of carbohydrate degradation under certain specific conditions, it was thought advisable to determine the stability of these compounds under the conditions of this series of experiments (1). The amounts of these substances indicated in the table were subjected to the action of oxygen in the presence of iron pyrophosphate solution at a temperature of 50° C. for a period of one to sixteen days.

In each set of experiments four control tubes were used, and the average change in weight of the control tubes was used as a correction factor. Hence the values given in the tables represent the average net change in the weight of the experimental tubes. In general, the procedure was the same as that reported in the previous papers (1 and 2).

[1] (From the Chemical Laboratory, Purdue University, Lafayette, Indiana.)

(1) J. Biol. Chem. 94:423 (1931); 95:409 (1932).

The data obtained for carbon dioxide formation in this set of determinations appear in the following table:

CO_2 PRODUCTION FROM ETHYL ALCOHOL, ACETALDEHYDE, ACETIC ACID, AND SODIUM ACETATE

Time in days		1	2	5	8	12	16
3.84 gm. Ethyl alcohol (Theoretical for CO_2 is 7.35 gms).	CO_2 obtained, gms.	—.0004	—.0004	—.0007	—.0011	—.0021	—.0022
	C returned as CO_2, %	—.006	—.006	—.009	—.015	—.028	—.028
	Determinations made	18	15	12	9	6	3
3.67 gm. Acetaldehyde (Theoretical for CO_2 is 7.35 gms).	CO_2 obtained, gms.	—.0006	—.0009	+.0025	+.0232	+.0603	+.1366
	C returned as CO_2, %	—.008	—.012	+.034	+.316	+.822	+1.863
	Determinations made	18	15	12	9	6	3
5.01 gm. Acetic Acid (Theoretical for CO_2 is 7.35 gms).	CO_2 obtained, gms.	—.0044	—.0080	—.0087	—.0096	—.0034	—.0019
	C returned as CO_2, %	—.060	—.109	—.119	—.131	—.046	—.026
	Determinations made	18	15	12	9	6	3
11.36 gm. Sodium Acetate (Theoretical for CO_2 is 7.35 gms).	CO_2 obtained, gms.	.0000	.0000	—.0014	—.0008	—.0013	+.0018
	C returned as CO_2, %	.000	.000	—.018	—.010	—.018	+.024
	Determinations made	18	15	12	9	6	3

From a study of the data given in the above table it is apparent that ethyl alcohol, acetic acid, and sodium acetate do not yield carbon dioxide under the conditions of these experiments. Titrations for total acid production and for volatile acid constituents likewise indicated the absence of oxidation. This is in agreement with the general behavior of these compounds and also agrees with the results obtained for the corresponding members of the one carbon series previously reported (2).

The experiments on acetaldehyde showed production of carbon dioxide, which definitely indicates oxidation. Titrations for total acid production led to the same conclusion. The study of the end products of this oxidation and the mechanism involved is reserved for a later paper. It is of interest to note, however, that acetaldehyde (supposedly present in the metabolic processes of the animal organism) is oxidized under the conditions of these experiments, whereas formaldehyde (which is poisonous to the animal organism) is not oxidized.

In conclusion it appears from the data obtained in this set of experiments that (1) ethyl alcohol, acetic acid, and sodium acetate are not oxidized by oxygen in the presence of iron pyrophosphates at 50° C., and (2) that acetaldehyde is oxidized under the conditions of these experiments, carbon dioxide being one of the end products.

(2) J. Biol. Chem. 95:409 (1932).

CONCERNING THE USE OF NITRO COMPOUNDS AS OXIDIZING AGENTS

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The use of nitro compounds as oxidizing agents upon aromatic side chains presents a type of double decomposition in which each of the reacting substances yields products of value. Thus if it were possible to oxidize the side chain of an aromatic alcohol, such as benzyl alcohol, the possible products would be benzaldehyde or benzoic acid on the one hand and azoxybenzene, azobenzene, hydrazobenzene or aniline on the other. If nuclear substitution products of nitrobenzene were used, such as the three nitrotoluenes—nitroanisoles, nitrophenetoles, dinitrobenzenes, etc, corresponding derivatives would be anticipated. The products formed and the amounts of each would depend upon temperature, pressure, acidity or alkalinity of the reacting medium.

Experimental

Lyons and Smith[2] state that azobenzene is the chief product formed by autoclave reduction of nitrobenzene with sodium benzylate. These experiments have been repeated, using instead of the autoclave a three-necked flask equipped with a mercury seal stirrer, reflux condenser and dropping funnel. This apparatus permitted thorough and continuous stirring of the reacting materials. The use of xylene as a solvent was found helpful. The nitrogenous product was found to consist of a mixture of azoxybenzene and azobenzene, the greater per cent in most instances being azoxybenzene. In these experiments the sodium hydroxide and the benzyl alcohol were mixed in a three-necked flask and heated gently to facilitate the formation of sodium benzylate. After cooling the nitrobenzene was added dropwise, followed by the xylene. The amount of xylene required to bring about suitable consistency for stirring was 40 cc. The temperature was then slowly raised to 138-140° C. by means of a paraffin bath. The results of these experiments are as follows:

Table I

NaOH Gms.	Azoxy-azobenzene Gms.	Azoxy-azobenzene Yield %	Benzoic Acid Gms.	Benzoic Acid Yield %
3	7.19	64.69	7.26	64.37
5	8.52	69.73	8.61	76.87
6	9.58	78.36	9.18	81.96
7	9.18	75.12	9.98	89.51
8	9.05	73.85	9.32	83.19
9	9.16	74.94	9.83	87.77
10	9.01	73.78	9.90	88.39
11	9.27	75.86	9.86	87.99

[1] This paper is an abstract of a thesis for a Ph.D. degree at Indiana University.

[2] Lyons and Smith, J.A.C.S. 48:3156 (1926).

In determining the respective percentage yields of azoxybenzene and of azobenzene the method suggested by Snowden,[2] using the melting points of mixtures of known composition, was found to be satisfactory. The original article of Snowden did not contain the melting point of various mixtures of azoxybenzene and azobenzene, but this information was secured from a study of the same made by Fry and Cameron.[3] The melting points of mixtures of azoxybenzene and azobenzene obtained in four different experiments were determined and the respective percentages ascertained from the data of Fry and Cameron.

Table II

Azoxybenzene and Azobenzene Gms.	M. P. °C.	Azoxybenzene %	Azobenzene %	Azoxybenzene Gms.	Azobenzene Gms.	NaOH Gms.	Benzoic Acid Yield %
9.13	34.9	99.19	0.81	9.06	0.07	8	93.39
9.00	34.0	97.75	2.25	8.80	0.20	9	96.51
8.98	33.9	97.59	2.41	8.76	0.22	10	88.66
9.27	34.5	98.55	1.45	9.14	0.13	11	89.73

Tests of the steam distillates for benzaldehyde with Schiff's reagent were positive and those for aniline by the isonitrile reaction were negative in each experiment.

In a study of the action of sodium methylate upon nitrobenzene Fry and Cameron (loc. cit., p. 864) state that the increase of molar concentrations of pyridine, which is decidedly basic, promotes the acidic dissociation of sodium hydroxide, thereby increasing the extent of the reduction of nitrobenzene by sodium methylate. Furthermore, that pyridine, because of its marked property for forming salts and a great variety of unstable molecular compounds, lends support to the idea that it may function as a carrier of positive hydrogen ions and negative ONa ions, thereby facilitating the reaction: $CH_3\ OH + HONa \rightarrow HCOONa + 2H_2$. From analogy it would seem that pyridine might also have a favorable influence upon the extent of the reduction in the reaction under investigation. Accordingly, a study of the effects of concentrations of one-half mole and one mole of pyridine upon the reaction of nitrobenzene and benzyl alcohol was made.

Table III

Reaction mixture: benzyl alcohol, 10 gms.; nitrobenzene, 12 gms.; sodium hydroxide, 9 gms.; xylene, 50 cc.; temperature, 138-140°C.; time, 4 hours.

Pyridine	Azoxybenzene and Azobenzene Gms.	Yield %	Benzoic Acid Gms.	Benzoic Acid Yield %
½ Mole	7.75	63.42	7.60	67.85
1 Mole	4.80	39.28	5.69	50.80
None	9.27	75.86	9.71	86.70

[2] Snowden, J. Phy. Chem. 15:797 (1911).

[3] Fry and Cameron, J.A.C.S. 49:869 (1927).

Under the conditions employed it is to be noted that the presence of pyridine results in a decrease of both azoxybenzene and benzoic acid.

The Three Isomeric Nitrotoluenes and Benzyl Alcohol

In continuing the study of the oxidation of benzyl alcohol with nitro compounds the three nitrotoluenes were used. The use of o-nitrotoluene as an oxidizing agent upon benzyl alcohol has been studied by Lyons and Smith (loc. cit., p. 3167), who report that the autoclave reduction yielded o-azotoluene and benzoic acid. The experimental work of this part concerns a study of the other two isomeric nitrotoluenes as well as a repetition of the experiments of Lyons and Smith using the open apparatus equipped with a stirrer.

p-Nitrotoluene and Benzyl Alcohol

The first experiment involved placing in the three-necked flask 10 grams of benzyl alcohol, 9 grams of sodium hydroxide, and 25 grams of p-nitrotoluene dissolved in 50 cc. of benzene. No reaction was noted at room temperature, so the flask and contents were heated by means of a water bath until the boiling point of the mixture was reached. The reaction mixture was kept at 83-85° C. during the first three hours and at 95° C. for the last three. The weight of the residue from the steam distillation was 12.34 grams. The benzoic acid amounted to 11.29 grams, which corresponds to a 100 per cent yield. The residue from the steam distillation was orange yellow in color and consisted principally of p-azoxytoluene. The melting point of the crude product was 70-75° C. The melting point of pure p-azoxytoluene as recorded in the literature is 70° C.

The experiment was repeated under the same conditions, except the amount of sodium hydroxide was reduced to 6 grams. A greater yield of p-azoxytoluene was obtained, 14.05 grams, corresponding to a 68.78 per cent yield. The yield of benzoic acid was 100 per cent.

o-Nitrotoluene and Benzyl Alcohol

The reaction mixture consisted of 5 grams of benzyl alcohol, 4.5 grams of sodium hydroxide, 12.5 grams of o-nitrotoluene mixed with 30 cc. of benzene. The contents of the flask were heated to the boiling point of the mixture, 85-90° C., for seven hours. During the heating period the mixture turned light yellow in color, which changed to a reddish purple on steam distillation. The o-azotoluene which was formed was separated from the alkaline sodium benzoate solution by means of a freezing mixture. The weight of the o-azotoluene was 4.02 grams corresponding to a 42.0 per cent yield. A portion of the o-azotoluene was crystallized from alcohol in the form of red needles, M. P. 55° C. The weight of the benzoic acid was 3.78 grams, or a 72.83 per cent yield.

m-Nitrotoluene and Benzyl Alcohol

In this experiment 4.5 grams of sodium hydroxide were used, 3 grams of which were added at the beginning and 1.5 grams after one-half of the reaction time had elapsed. The reaction was conducted at

the boiling point of the mixture. The residue from the steam distillation was light yellow in color, melted at 32-36° C. and weighed 5.80 grams. The melting point of pure m-azoxytoluene is 37-39° C. Traces of either m-hydrazotoluene or m-azotoluene in this product may be responsible for the lower melting point. The weight of the benzoic acid was 3.55 grams, which represents a yield of 68.4 per cent. The yield of the m-azoxytoluene was 62.56 per cent.

The Three Isomeric Nitroanisoles and Benzyl Alcohol

The sodium benzylate and the nitro compound were allowed to react at room temperature for three hours, after which they were heated to 100° C. for an additional two hours. The reduction compounds were all of a yellow color and turned deep red, which is characteristic of the azo compound, when subjected to further reduction by means of iron and hydrochloric acid. The melting points of the compounds were determined and compared with those recorded in the literature.

Table IV

Reaction mixture: 5 gms. of nitro compound; 50 cc. xylene; 3 hours at room temperature and 2 hours at 100°C.

Nitro Compound	Gms. Alcohol	Gms. NaOH	Gms. Azoxy Comp'd	% Azoxy Comp'd	M. P. Azoxy Comp'd	Gms. Benzoic Acid
o-Nitroanisole*	10	8	5.9	53.8	85-86°C.	4.5
m-Nitroanisole	10	8	3.2	76.0	51-52°C.	2.95
p-Nitroanisole	10	8	2.9	68.8	116.5-118°C.	3.30

*13 gms. of the ortho compound was used in this experiment.

An experiment was made with o-nitroanisole in which the alkalinity was increased to 15 grams, other conditions remaining the same, whereby the yield of the o-azoxyanisole was increased to 4.5 grams corresponding to a 95.0 per cent yield.

The Three Isomeric Nitrophenetoles and Benzyl Alcohol

The following table gives the results of these experiments:

Table V

Reaction mixture: 5 gms. of nitro compound; 50 cc. of xylene; 3 hours at room temperature and 2 hours at 100°C.

Nitro Compound	Gms. Alcohol	Gms. NaOH	Gms. Azoxy Comp'd	% Azoxy Comp'd	M. P. Azoxy Comp'd	Gms. Benzoic Acid
o-Nitrophenetole	5	5	3.5	76.4	101°C.	1.28
m-Nitrophenetole	5	5	3.1	67.6	46-47°C.	1.36
p-Nitrophenetole*	10	8	6.3	55.6	135°C.	4.00

*13 grams of the para isomer was used in this experiment.

An experiment was made with o-nitrophenetole in which the alkalinity was increased to 15 grams, other conditions remaining the same, whereby the yield of the o-azoxyphenetole was increased to 4.5 grams corresponding to a 98.2 per cent yield.

m-Dinitrobenzene and Benzyl Alcohol

The possibilities of the formation of intermediate products are still more extended with the presence of two nitro groups on the benzene ring. Lyons and Smith (loc. cit., p. 3166) report that m-dinitrobenzene and benzyl alcohol react producing ammonia and a charred mass when the experiment is carried out in the autoclave at a temperature of 138-140° C. Conditions have been found which permit the reaction to proceed under control without the decomposition of the organic material.

Ten grams of benzyl alcohol were placed in a three-necked flask. Eight grams of sodium hydroxide were added to the reaction mixture in portions of one gram each at intervals of one-half hour. A solution of 10.4 grams of m-dinitrobenzene in 50 cc. of xylene was added dropwise to the mixture at room temperature. The heat of reaction of the two substances was sufficient to keep the temperature at approximately 50° C. The experiment was run for five and one-half hours. After the initial heat of reaction had subsided the temperature was maintained at 30° C. At the end of the heating period the light brown mixture was steam distilled. The weight of the air-dried residue was 7.78 grams. A portion of the residue was dissolved in hot benzene, from which it separated as a pale yellow non-crystalline mass, M. P. 228-233° C. The melting was proceeded by shriveling and accompanied by slight decomposition. A portion of the substance dissolved in hot glacial acetic acid was heated to boiling for fifteen minutes with a small portion of chromic acid. The mass which separated from the cooled mixture was washed several times with ether to free it from the acids and dissolved in hot toluene, from which it separated as a light yellow flocculent precipitate. The dried substance was a pale yellow powder melting at 239-241° C. (I). Solution of the substance in hydrochloric acid and treatment with sodium nitrite showed the compound free from amino groups.

A quantitative determination of the nitrogen in the compound gave the following data: 0.1335 grams of the substance gave 25.2 cc. of nitrogen at 27.0° C. and 747.5 mm. = 20.63 per cent.

It was surmised that some of the nitrogen was present as unreduced nitro groups and that the compound under investigation was a dinitrohydrazo compound of the formula $C_{12}H_{10}N_4O_4$ (N = 20.43 per cent) and a molecular structure 3-3^1-O_2N-C_6H_4-NH-NH-C_6H_4-NO_2.

The compound was subjected to further reduction by boiling with a mixture of 50 cc. of ammonium hydroxide and 50 cc. of ammonium hydrosulphide for two hours. At the end of the heating period the mixture was filtered and water added to the filtrate to cause the precipitation of the reduction product. The substance, twice crystallized from alcohol, was found to melt sharply at 145°C. The crystals which grew from the alcohol were long yellow needles which were almost insoluble in water and ether and readily soluble in alcohol. The substance

3-3¹-diaminohydrazobenzene, M. P. 151° C., described in the literature was found in exact agreement with the above preparation with the exception of the slightly higher melting point. The general deportment and the analytical data are such that the identity of the compound (I) is established as 3-3¹-dinitrohydrazobenzene, a substance not heretofore described in the literature.

A balanced equation accounting for all products of this reaction may be written as follows:

$$4C_6H_5CH_2OH + 2C_6H_4(NO_2)_2 \rightarrow C_6H_5\text{-}COOH + 3C_6H_5CHO + O_2N\text{-}C_6H_4\text{-}NH\text{-}NH\text{-}C_6H_4\text{-}NO_2 + 3H_2O$$

Since it was not possible to heat the reaction mixture above 100° C. on account of the decomposition, benzene instead of xylene was used as the solvent for the m-dinitrobenzene. Heating the reaction mixture to 70° C. after the initial heat of reaction had subsided was found to increase the yield of both the benzoic acid and the 3-3¹-dinitrohydrazobenzene. The following table shows the effect of heating reaction mixtures of the same composition for different lengths of time at 70° C. In all of the experiments the sodium hydroxide was added in portions of one gram at intervals of one-half hour.

Table VI

Reaction mixture: benzyl alcohol, 10 gms.; m-dinitrobenzene, 8 gms.; sodium hydroxide, 8 gms.; benzene, 70 cc.; temperature 70°C. after initial heat of reaction had subsided.

Hours at 70°C.	3-3¹-Dinitro-hydrazobenzene Gms.	Yield %	Benzoic Acid Gms.	Benzoic Acid Yield %
1½	4.17	64.1	6.15	63.40
2	4.80	73.8	6.90	61.60
6	5.10	97.7	9.52	85.00
8	6.65	86.65	7.68	68.57

In the next group of experiments the amount of sodium hydroxide was increased to 19.5 grams and the time during which the reaction mixture was heated to 70° C. was made the variable factor.

Table VII

Reaction mixture: benzyl alcohol, 10 gms.; m-dinitrobenzene, 12.6 gms.; sodium hydroxide, 19.5 gms.; benzene, 70 cc.; temperature, 70°C. after the initial reaction had subsided.

Hours at 70°C.	3-3-Dinitro-hydrazobenzene Gms.	Yield %	Benzoic Acid Gms.	Benzoic Acid Yield %
6	8.65	84.22	10.63	94.91
7	7.15	69.62	10.29	91.87
8	6.94	67.57	10.57	94.37

SUMMARY

1. The study of the reactions of sodium benzylate with aromatic nitro compounds as oxidizing agents has been extended to include o-, m-, p-nitrotoluene, o-, m-, p-nitroanisole, o-, m-, p-nitrophenetole and m-dinitrobenzene.

2. Optimum conditions have been found for obtaining the maximum percentage yields of benzoic acid and of the respective azoxy-, azo-, or nitrohydrazocompounds.

3. The preparation and properties of the new compound, 3-3¹-dinitrohydrazobenzene, are reported.

DETERMINATION OF THE DEGREE OF HYDRATION OF MAGNESIA IN DOLOMITIC LIMES

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Hydrated limes made from dolomites quarried at Woodville and Gibsonburg, Ohio, are plastic, and hydrated limes made from dolomites quarried at all other places are not plastic. No reason for this unusual and valuable property of the Ohio dolomites has ever been discovered. All experiments and experiences indicate that this property depends in some way upon the magnesia.

At the plastic lime plants in Ohio the greatest care is taken to burn the lime at the lowest possible temperature. Too high a temperature is known to prevent the plastic property. No other single factor in manufacturing seems important inasmuch as all the other factors or conditions such as type and size of kiln, kind of fuel, type of hydrator, quantity of water used in hydration, and type of mill for final grinding are different in the different plants. On the other hand, no one has been able to burn any rock other than from this Ohio district into a plastic finishing hydrate in the ordinary commercial kilns. The scientific reason for this unusual quality of the Ohio finishing limes is interesting both in theory and in practice.

The low temperature of burning of these Ohio limes without doubt produces active magnesia. Campbell[2] showed that magnesia made by burning magnesium carbonate at 1000° C. hydrated to the extent of 18 per cent in one day, but if it was made at a temperature of 1100° the hydration dropped to 7 per cent, and if burned at 1200° the hydration was only 0.43 per cent. Johnston[3] found that magnesite decomposed at 756° and calcium carbonate rock at 898°. Artificially made magnesium carbonate decomposed at a lower temperature. A natural dolomite de-

[1] A portion of the thesis submitted by Mr. Fox for the Ph.D. degree at Indiana University in 1927. Delay in publication was due to the death of Mr. Fox.

[2] Jour. Ind. Eng. Chem., 1:665 (1909).

[3] J. Amer. Chem. Soc., 32:938 (1910).

composed at a lower temperature. A natural dolomite decomposed at about 835°, which indicated that the dolomite tested was a compound of magnesium and calcium carbonate and not a mixture of the two. In commercial burning of the dolomitic lime the temperature must be high enough to decompose the calcium carbonate also.

High temperature, besides affecting the magnesia, causes chemical combinations between the magnesium, calcium and iron oxides and the silica and alumina forming silicates and aluminates. The effect of this reaction may be very important, although it has not been considered by anyone as having an effect on plasticity.

A determination of the quantity of water with which the magnesium oxide combines or with which it can be made to combine is an accurate measure of the activity of the magnesia. Richardson's[4] thermal method of determining the hydrated magnesia in the hydrated lime is based upon the fact that magnesium hydroxide loses its water and becomes anhydrous at a much lower temperature than does calcium hydroxide or other constituents in the lime. He judged the temperature of decomposition of the magnesium hydroxide from breaks in "temperature loss in weight" curves made by plotting the weights of the samples heated for twenty-minute periods at regularly increased temperatures. His conclusion from ten different hydrated limes was that there was no relation between the per cent of magnesium hydroxide and the quality or commercial value of the lime. For example, two non-plastic hydrates showed 19.5 and 13.9 per cent of their magnesia present as the hydroxide, while a plastic hydrate from Woodville showed 10.7 per cent. It is possible that the age of the samples may have given the magnesia a chance to hydrate during storage. All freshly manufactured hydrates in the table did show lower degrees of hydration.

The object of this research was to determine the quantity of unhydrated magnesium oxide in the hydrated lime which would hydrate or react with water if soaked with water over night. This soaking over night is necessary commercially to develop the plasticity of the plastic Ohio hydrated limes. It was thought that the special properties of the plastic limes might be due not to the quantity of magnesium hydroxide in the original dry hydrated lime as determined by the method of Richardson but to the additional magnesium hydroxide which formed during the usual soaking preparatory to its use. Richardson showed in one sample that soaking increased magnesium hydroxide from 7.2 per cent to 11.9 per cent.

METHOD OF ANALYSIS

The samples of hydrated limes were weighed into porcelain boats which were placed inside large Pyrex tubes containing pans of calcium oxide. These tubes were then heated in an electric furnace. The purpose of the calcium oxide was to absorb carbon dioxide from any air which might leak into the tube and to absorb the water evolved by the sample when heated. This procedure was easier than that of Richardson in which a very rapid current of pure air was passed over the

[4] Jour. Amer. Chem. Soc., 19:625 (1927).

samples in the tubes. The samples were first dried at 105° to remove simple extraneous moisture. Then they were dried at 360° to determine the water already combined with magnesium oxide from which the hydrated magnesia in the limes was calculated. The samples were then moistened with distilled water and, after twelve hours, were dried at 105° to a constant weight. They were then heated at 360° to a constant weight. The difference between these two weights gave the total hydrated magnesia. Subtraction of the hydrated magnesia originally present from this total value gave the hydrated magnesia which was formed by the soaking. The plasticity numbers are given in the table and the limes are arranged in the order of decreasing plasticities.

Plasticity	Per cent magnesia already hydrated	Per cent magnesia hydrated during soaking
296	14.3	16.5
180	6.9	9.1
172	8.1	14.1
166	8.6	6.6
150	11.1	16.6
147	4.6	18.1
128	2.7	14.7
106	2.8	10.8
55	4.8	11.

Numerous experiments upon limes burned in the laboratory at various temperatures and under varying conditions showed that the magnesia hydrated to a greater extent the lower the temperature and the shorter the time of heating. A survey of all the results shows no regularity between plasticity and the magnesium hydroxide present either in the original lime or formed during soaking.

POSSIBLE SOURCES OF ERROR

A. The soaked samples were dried at 105° for weighing, whereas in regular commercial work hydrated limes are soaked without any heating. It may have been that the heating during drying caused the magnesia in the non-plastic hydrates to react with water about as completely as did the plastic limes. No way could be devised to avoid this possible error.

B. It may be that silicates and aluminates as well as magnesia react with water and lose water when dried at 360°. However, only small quantities of such compounds are possible because most limes tested contained less than one per cent of such impurities.

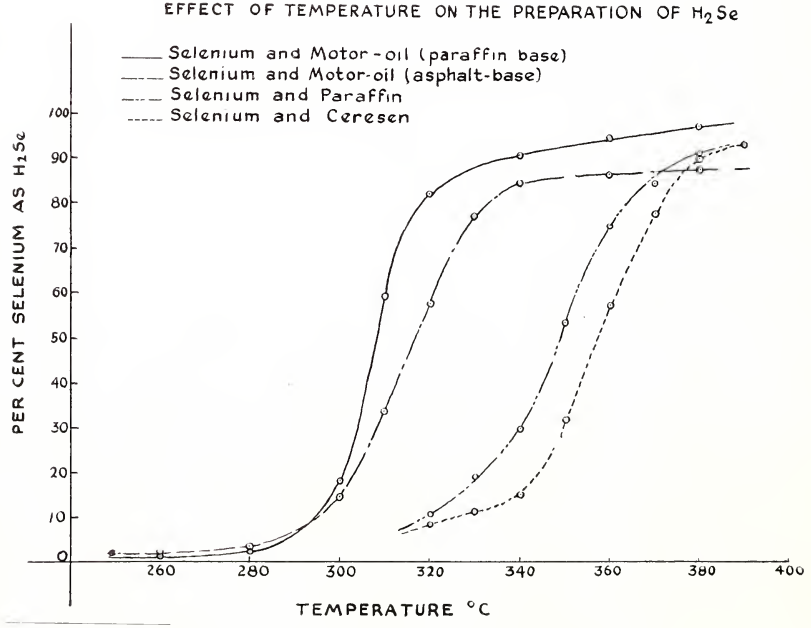
THE PREPARATION OF HYDROGEN SELENIDE BY THE INTERACTION OF SELENIUM AND HYDROCARBONS

CLARENCE GREEN[1] and W. E. BRADT,[2] State College of Washington

Graefe[3] and Siebeneck[4] reported the formation of hydrogen selenide when selenium was heated with lubricating oil (3) and paraffin (4). E. D. Scudder and R. E. Lyons[5] completed a systematic study of the formation of hydrogen sulfide by a similar reaction in which they obtained a maximum yield of 70 per cent H_2S.

The authors have investigated some of the factors affecting the preparation of hydrogen selenide.

Procedure. In each experiment one gram of powdered selenium was placed with 50 grams of hydrocarbon in a 150 cc. Pyrex flask. The flask was connected to a source of hydrogen and to an absorption apparatus containing aqueous NaOH. Temperature was controlled by means of an insulating jacket and was observed by means of a copper-nichrome thermocouple.



[1] Graduate student in chemistry.
[2] Assistant Professor of Chemistry.
[3] Z. angew. Chem. 34:509 (1921).
[4] Petroleum Zeit. 18:281 (1922).
[5] Proc. Ind. Acad. Sci. 40:185 (1930).

Prior to beginning each experiment all air was washed out of the apparatus and solutions by the passage of hydrogen for 15 minutes. At the completion of each heating period (one hour) all H_2Se was washed into the absorbing solution by the same process.

At this point the absorbing solution was diluted, treated with sodium peroxide, acidified with HCl, and saturated with sulfur dioxide. The precipitated selenium was then determined gravimetrically.

Experimental Data. The following table is self explanatory:

TABLE I

Heating period: 60 minutes
Selenium: 1.000 g. powdered
Yield: Based on selenium

Hydrocarbon (50 g.)	Temperature (° C.)	Yield H_2Se (%)
Paraffin (*a*)	320	10.5
"	330	18.9
"	340	29.7
"	350	53.0
"	360	74.6
"	370	83.7
"	380	90.2
Ceresin (*b*)	320	8.7
"	330	11.8
"	340	15.1
"	350	31.5
"	360	57.0
"	370	77.6
"	380	90.1
"	390	92.5
Motor Lubricant (*c*)	260	1.9
" "	280	3.5
" "	300	14.6
" "	310	33.4
" "	320	57.8
" "	330	76.5
" "	340	84.0
" "	360	86.0
" "	380	87.1
Motor Lubricant (*d*)	260	1.7
" "	280	2.7
" "	300	18.0
" "	310	59.0
" "	320	81.6
" "	330	87.1
" "	340	90.5
" "	360	94.2
" "	380	96.8

Motor Lubricant (*e*)	320	46.4
" "	340	79.6
Motor Lubricant (*f*)	340	31.5
" "	350	67.2

(*a*) M. P. = 60° C.
(*b*) Technical (White) Eimer and Amend.
(*c*) Asphalt Base (Zerolene No. 5).
(*d*) Paraffin Base (Standard Aviation Oil).
(*e*) Same as (*d*), previously heated for 1 hr. with 1 g. of selenium.
(*f*) Same as (*d*), previously heated for two 1 hr. periods with 1 g. of selenium each period.

Summary. Hydrogen selenide is obtained by heating powdered selenium with high boiling hydrocarbons. A maximum yield of 96.8 per cent H_2Se (based on the selenium used) was obtained by heating 50 g. of a paraffin base motor oil with 1 g. of selenium for one hour at 380° C.

Heating the same 50-gram portions of a paraffin oil with repeated additions of selenium (1 g. each) reduced the formation of H_2Se to approximately that obtained by the use of paraffin at corresponding temperatures.

In contrast with the results obtained by E. D. Scudder and R. E. Lyons with hydrogen sulfide the yield of hydrogen selenide increases with increased temperatures. Only negligible yields were obtained below 300° C.

ANALYSIS OF GROUP III

RALPH W. HUFFERD, Greencastle

Since reporting a paper under the same title to this group eleven years ago several changes have been introduced into the scheme. In conversation with instructors and students in other laboratories the writer still hears the common complaint that cobalt and zinc are prone to give trouble. It has been our experience that the careful student has trouble with neither of these.

As reported before (1) the main departure from the generally accepted scheme of analysis lies in the very strenuous treatment of the group precipitate at the time of separating it into divisions. Detection of cobalt has been made certain and easy by a modification of the Morrel-Vogel test (2). Since the difficulty with detection of zinc lies in the confirmatory test, unless it has been left in the Iron Division precipitate, it has been found expedient, especially for the beginning student, to employ two confirmatory tests. One of these, the ferrocyanide test, has been modified to meet all conditions.

The scheme has been worked out with both speed and accuracy in mind. Almost all filtrations are carried out by suction. Solutions are

prepared to permit the use of ordinary qualitative filter paper. If the importance of permitting precipitates to settle out and of pouring off the supernatant liquid is sufficiently emphasized all filtrations can be done by suction, thus saving considerable time.

Separation into Divisions

The group precipitate is dissolved by addition of 3N hydrochloric acid and boiling. If necessary (cobalt or nickel present) the minimum amount of nitric acid is added. No attempt is made to separate the precipitate from the paper before carrying out this step. A little hot water is added and the solution sucked off from the paper pulp and sulfur.

While the solution is still hot 30 per cent sodium hydroxide is added with stirring until a precipitate forms and persists, or, if no precipitate forms, until the solution is strongly alkaline. If there is a precipitate a further excess of 5-10 cc. of 30 per cent sodium hydroxide is added. About half a gram of sodium carbonate is added and put into solution.

The solution or suspension is then cooled somewhat and 1-3 g. of sodium peroxide added a little at a time with stirring. After 2 minutes boiling 2 volumes of hot water is added and boiling continued for 3 minutes. The precipitate is then filtered off without cooling and thoroughly washed with hot water.

Aluminium Division

The combined filtrates are treated in the customary manner to remove aluminium and to test for chromium. Due to the previous use of concentrated hot alkaline solution care must be taken to differentiate between aluminium hydroxide and silicic acid. The use of alizarin has been quite satisfactory.

If the solution does not contain chromium 5 drops of dichromate solution is added to the filtrate from the aluminium hydroxide. Whether or not it has been necessary to add dichromate, acetic acid is added until the chromate yellow turns to dichromate orange. 5 cc. of saturated hydrogen sulfide water is now added. If zinc is present a flocculent precipitate of zinc sulfide will form at once. Colloidal sulfur will also appear, but more slowly. Three suction filtrations through the same filter are sufficient to remove all of the sulfide along with a little sulfur. The filtrate will be milky. The precipitate should be washed with 10 cc. of hot water.

A hot solution of 2 cc. of 6N hydrochloric acid in 10 cc. of water is then sucked through the filter two or three times and boiled to remove hydrogen sulfide. Excess ammonia is added to the cooled filtrate and followed by a slight excess of acetic acid. The solution is divided into two portions in small test tubes. To one portion 2 drops of potassium dichromate solution is added followed by 5 drops of potassium ferrocyanide solution. A white precipitate is zinc ferrocyanide. To the other portion 2 cc. of hydrogen sulfide solution is added. A white precipitate is zinc sulfide.

IRON DIVISION

Without separation from the paper the precipitate is placed in a casserol and 15 cc. of hot 6N nitric acid is added. This treatment either dissolves the precipitate or so loosens it that the paper can be removed and washed with a little 6N nitric acid, which is then added to the contents of the casserol. The solution is evaporated to 10 cc. or less. After adding 10 cc. of 16N nitric acid and boiling for a minute the casserol is removed from the flame. The solution (if manganese is absent or if peroxide has not been carefully washed out) or suspension is permitted to cool slightly and then 0.5 g. of potassium chlorate is cautiously added in small quantities with stirring. After gentle boiling another half gram of chlorate is added and the boiling repeated. This treatment should normally completely precipitate the manganese as the brown or black oxide.

If there is no precipitate the solution is again evaporated to half volume and 5 cc. 16N nitric acid added and followed by more chlorate. After a moment's boiling 20 cc. of water is added and the precipitate filtered off without cooling.

Iron is removed in the customary manner.

The ammoniacal filtrate from the ferric hydroxide is boiled until the odor of ammonia is weak but noticeable. A portion of it is tested for nickel with dimethylglyoxime.

The remainder is evaporated to a syrupy consistency but not to dryness; transferred to a test tube while still hot; cooled; enough water added to put almost all of the solid into solution; and 3 cc. 10 per cent potassium thiocyanate solution added. 3 cc. of a 1:4 mixture of isoamyl alcohol and ethyl ether is poured in and gently shaken. A blue-green color in the ether layer is proof of the presence of cobalt. A colorless layer is proof of its absence. If the color is indistinct due to the presence of a trace of iron a drop of 12N hydrochloric acid added from the point of a pipette to the surface of the ether layer will produce the distinct blue-green color if cobalt is present.

MODIFICATIONS

If *oxalate* is present there is no modification of the scheme until after the removal of manganese. Since manganese dioxide cannot precipitate until oxalic acid has been destroyed its appearance can be taken as evidence of the destruction of the oxalic acid. If manganese is absent 2 cc. of manganese nitrate solution is added and the oxide thrown out by treatment with nitric acid and chlorate.

The filtrate is made ammoniacal and hydrogen sulfide passed in. The filtrate after this treatment is added to the original filtrate from the Group III precipitate. The precipitate is dissolved in dilute nitric acid and the resulting solution freed from sulfur. It is ready for precipitation of ferric hydroxide as in the ordinary scheme.

If *phosphate* is present after testing for manganese as usual test not more than 1/5 of the filtrate for iron by adding ammonia. A red precipitate indicates iron, but should be filtered off, dissolved in 6N hydrochloric acid and tested with thiocyanate and with ferrocyanide. The

filtrate from the red precipitate should be returned to the remaining 4/5 of the filtrate from manganese dioxide.

Following the customary procedure phosphate is removed by adding ferric nitrate, unless iron is present in considerable amount, and throwing it out as the phosphate and basic acetate.

The phosphate and iron free filtrate is made ammoniacal and treated with hydrogen sulfide. The sulfides of cobalt and nickel are filtered off and the filtrate returned to the filtrate from Group III.

The black precipitate is covered on the paper with 6N hydrochloric acid and a few drops of 6N nitric acid added. After filtering and washing the residue, the filtrate is made ammoniacal and treated as though it were the filtrate from ferric hydroxide in the regular scheme.

DISCUSSION OF RESULTS

The following table indicates the accuracy of the scheme under varying conditions.

Milligrams of the Atom

Zn	Cr	Mn	Fe	Co	Ni	Al
—	—	9	9	1.8	9	—
—	—	3.6	3.6	3.6	18	—
—	—	1.3	13.3	.7	13.3	—
—	—	2	100	1	100	—
5	—	—	250	—	—	—
5	—	250	—	—	—	—
5	—	250	250	—	—	—
5	—	500	500	—	—	—
5	—	500	500	2	3	—
5	8.5	500	500	2	3	—
.5	—	1	—	.5	5	—
.5	17	18	20	10	5	—
2	—	500	500	1	10	10
10	—	100	100	2	100	100
10	100	100	100	10	100	100

LITERATURE CITED

(1) Proc. Ind. Acad. Sci. 1922 (1923) p. 138.

(2) F. Morrel, Z. f. Anal. Chem., 16, 251, 1877.

ON THE PROGENITORS OF CERTAIN PLANT ALKALOIDS AND THE MECHANISM OF THEIR FORMATION IN THE PLANT STRUCTURE[1]

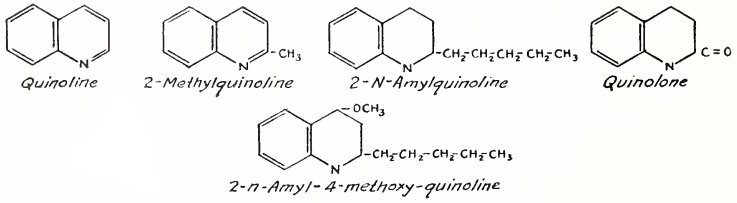
PERCY L. JULIAN, DePauw University

In this paper we desire to review briefly work of certain investigators aimed at discovery of precursors of plant alkaloids, and to outline, in a preliminary way, several experiments which have been in progress in this laboratory for some time, reserving experimental details for later publication when our work is completed.

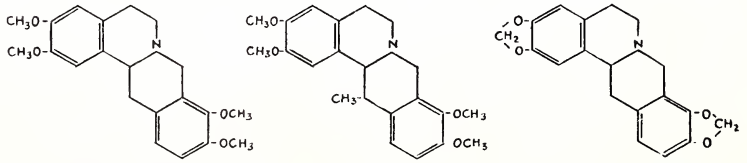
Two types of experimental work might be employed in attacking this problem. The first would comprise a careful isolation of the natural products found in any one plant to the end that substances occuring even in minute quantities might be isolated, for it is these substances which may prove to be intermediates in the synthetic processes of the plant. Such intermediates may point out the way which the plant takes in its synthesis of large molecules, and thereby throw light upon all the chemical happenings in the cell structure.

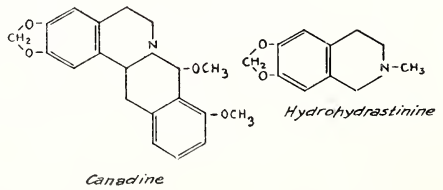
Work of this type has not often been done heretofore. In the realm of alkaloids, two plants which have been carefully investigated by Späth and his collaborators illustrate strikingly the possibilities in such work. One of these is the Angostura[2] and the other Corydalis.[3] In the former the quinoline nucleus predominates, in the latter the isoquinoline nucleus.

Späth and Pikl, for example, have isolated from Angostura the following alkaloids:



From *Corydalis cava* the following alkaloids were isolated:





[1] Preliminary communication.

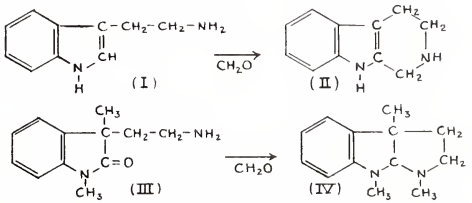
[2] Späth and Pikl, Ber. 62:2244 (1929); M. 55:352 (1930).

[3] Späth and Tröthandl, Ber. 56:875 (1923); Späth and Julian, Ber. 64:1131 (1931).

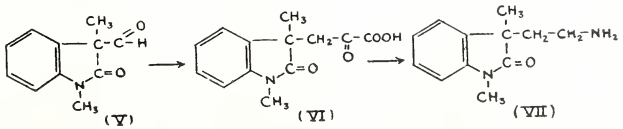
Our isolation of Hydrohdrastinine seems to me of significance for several reasons: 1. Let us recall that from the Cactus plant, for example, Homoamines of the type, $RCH_2CH_2NH_2$, have been isolated. In certain plants, then, these homoamines can exist, and it has been assumed that they are produced through enzymatic action from the corresponding amino-acids, $R\text{-}CH_2\text{-}CH(NH_2)COOH$. 2. Decker long years ago[5] showed that homoamines could be converted into N-Methyltetrahydroisoquinolines. Looking at the formula for Hydrohydrastinine, it seems reasonable to suppose that here we have one of the first substances which the plant produces in its synthesis of the isoquinoline alkaloids. In the one direction formaldehyde is polymerized to sugars, in the other it may be converted by homopiperonylamine into hydrohydrastinine.

The second type of experiment then which, in my opinion, should be more often carried out by present-day organic chemists, is an attempt to duplicate such syntheses as Decker carried out under physiological conditions. We can then be reasonably sure of our hypotheses as to the course taken by the plant. Such experiments have been carried out on Angostura alkaloids by Schöpf[6] who made good use of the results of Späth and Pikl on these compounds. Moreover, the organic chemist should seek to employ as far as is possible such methods of synthesis, even under "laboratory conditions," as the plant might take, and I wish to report in this connection in a preliminary manner certain of our experiments, in which we have attempted to do this.

In view of what has been said we may assume with a fair degree of certainty that the Homoamines and Formaldehyde are progenitors of the isoquinoline alkaloids, indeed of even the most complex ones. As further illustration let us take two classes of alkaloids, the Harmala Alkaloids (II) and those alkaloids of the Calabar Bean containing the Physotigmine Ring (IV). It is reasonable to suppose that (II) might very well be synthesized by the plant from (I) and (IV) from (III).



The first of these syntheses has been carried out in a manner similar to that which the plant would take[7] and we wish to describe experiments which have had as their objective the obtention of the amine (III), and ultimately the compound (IV). Certain stages in our synthesis may be represented by the following formulae:

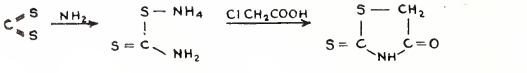


[5] Ann. **395**:345 (1913).

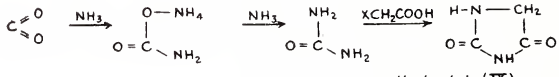
[6] Ann. **497**:1 (1932).

[7] Späth and Lederer, Ber. **63**:120 (1930).

In order to secure as much amine as possible from difficultly accessible aldehydes such as (V) we are compelled to work out a method which would yield homoamines in better yield than the methods hitherto employed have done. Such a method was found in Gränacher's reaction between the aldehydes and rhodanine, and we have recently reported this work[8]. At this time we wish to call attention to the biological significance of our Rhodanine condensations. The substance Rhodanine has the formula represented by (VIII) and our improved method prepares it quite readily from carbon disulphide, ammonia and chloracetic acid.



(VIII) *Rhodanine*



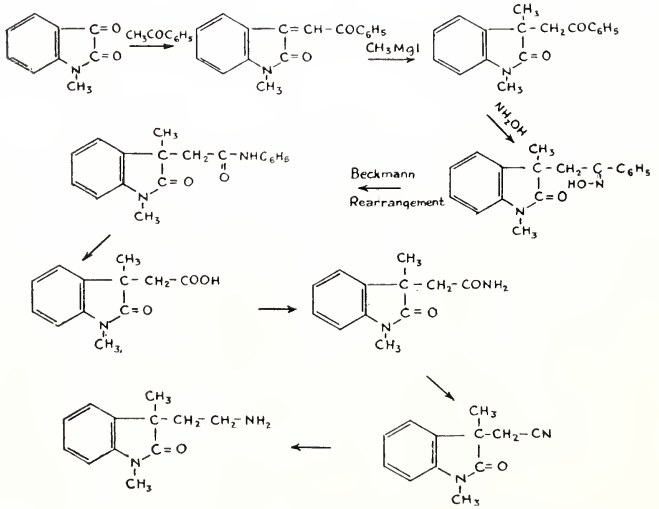
Hydantoin (IX)

It is possible for the plant to build up products exactly similar to Rhodanine (IX) and by a method paralleling that for Rhodanine. Condensation of aldehydes with a skelton like (IX) would exactly duplicate our condensations with Rhodanine and yield ketimino-acids of the general formula, $R\text{-}CH_2\text{-}C\text{-}COOH$, which Knoop and Oesterlin[9] have assumed as

$$\begin{matrix} & \| \\ & NH \end{matrix}$$

intermediates in their synthesis of amino acids.

As a means of checking the structures of our products produced by the above-mentioned synthesis, we have in progress another method for preparing the amine (VII).



[8] Julian and Sturgis—Read at Fall Meeting of Am. Chem. Soc., Chicago, Sept. 12, 1933.

[9] Zeit. für physiol. Chemie, 170:186 (1927).

Obviously this is an extravagant way which the plant would not take, but it involves certain types of reactions which have been studied in detail and indicates clearly the way in which such work may assist the "organic chemistry under biological conditions."

Our greatest difficulties up to the present time have been in securing in good yield certain of the basic substances in the synthesis of the amine (VII). The preparation of N-Methyl Isatin in large quantity had to be carefully worked out as the old Friedlander method does not give satisfactory results. Likewise the preparation of 1,3-Dimethyl Oxindole-3-Aldehyde (V) was secured in good yield only after numerous experiments. We have not yet been successful in obtaining smooth ring closure to (IV) but hope to report success in this direction when the complete experimental results are published. Our purpose in this review has been largely to stimulate interest in such work by reviewing briefly our own experiences and those of others.

SEPARATION OF IRON FROM INDIUM WITH CUPFERRON

FRANK C. MATHERS and CLARENCE E. PRICHARD, Indiana University

Experiments conducted some years ago upon the methods for the separation of iron from indium showed this separation to be difficult and unsatisfactory by any of the methods and they led to a new method based upon the precipitation of the iron with nitroso-B-naphtho[1]. More recently the use of cupferron as a reagent for the precipitation of iron, suggested the idea that it might be substituted advantageously for the nitroso-B-naphthol. Experiments by various authors[2] have shown that a six per cent solution of cupferron will completely precipitate iron, copper and certain other metals in hydrochloric acid solutions while aluminum remains in solution. Indium is so closely related to aluminum in the Mendeleeff Periodic Table that a similar behavior towards cupferron was to be expected.

Preliminary experiments with the cupferron method for precipitating iron showed that an error of 0.4 to 0.8 mg. was made when using 0.07 g. Fe_2O_3 as ferric chloride, 0.7 g. cupferron and 1 to 3 cc. of hydrochloric acid, in a total volume of 40 cc. Portions of an indium chloride solution to which portions of a standard ferric chloride solution were added, were precipitated with cupferron. The precipitates were ignited and weighed as ferric oxide (Fe_2O_3). The filtrates were precipitated with ammonium hydroxide and the residues thus obtained were ignited

[1] Mathers, This Jour., 30:209 (1908).

[2] Fresenius, Z. anal. Chem., 50:35 (also a review with references). Becculi and Grassi, Gazz. chim. ital., 43 I 570; through C. A. 7:1688.

Thornton, Am. J. Sci., (4) 37:137 and 407.

over Bunsen burners and weighed as indium oxide (In_2O_3). This residue of indium oxide showed from 0.07 to 0.12 mg. of ferric oxide (Fe_2O_3), the test being made by color comparison using potassium sulphocyanate.[3] The following table shows the results:

No.	In_2O_3 taken (g.)	Fe_2O_3 taken (g.)	HCl added (cc.)	Cupfer. added (g.)	Final volume of sol. (cc.)	Fe_2O_3 ppt. by cupfer. (g.)	In_2O_3 from filtrate (g.)	In_2O_3 lost (g.)
1	0.0606	none	2	0.24	16	0.0025	0.0598	0.0008
2	0.0606	0.0363	3	0.60	21	0.0387	0.0598	0.0008
3	0.0606	none	3	0.24	17	0.0009	0.0586	0.0020
4	0.0606	0.0726	3	0.60	33	0.0760	0.0587	0.0019
5	0.0606	0.0726	3	0.60	33	0.0721	0.0603	0.0003
6	0.0718	none	3	0.24	17	0.0018	0.0695	0.0023
7	0.0718	none	3	0.24	17	0.0009	0.0698	0.0020
8	0.0718	0.0726	3	0.60	33	0.0726	0.0690	0.0028

The method of Gooch and Havens[4] for the separation of aluminum from iron was tried for indium and iron. This method is based upon the fact that hydrous aluminum chloride ($AlCl_3.6H_2O$) is insoluble in a mixture of strong hydrochloric acid and ether saturated with hydrochloric acid gas, while ferric chloride is completely soluble. This method, tested with standard solutions of aluminum chloride and varying amounts of ferric chloride, showed an error on the aluminum of —0.2 to —0.8 mg. After this proof that the operation of the method was understood, experiments were undertaken with indium chloride solutions. In no case was it possible to obtain a precipitate of the indium chloride. The conditions were varied and a number of other organic liquids, e.g., chloroform, glacial acetic acid, and carbon tetrachloride, were tried, but no precipitate was obtained. The conclusion must be drawn that the properties of the elements of group III vary with increasing atomic weight to such an extent that the indium chloride is soluble although the aiuminum chloride is insoluble in a mixture of ether and hydrochloric acid saturated with hydrochloric acid gas.

SUMMARY

1. Cupferron will completely precipitate iron in the presence of indium.

2. There is a small loss in the quantity of indium. The cause of this loss was not investigated.

3. The precipitate of the iron with the cupferron filters easily and is not bulky like the precipitate with nitroso-B-naphthol, hence material containing a larger quantity of iron may be treated.

4. This method is considered the best for the complete purification of indium from small amounts of iron. The major portion of the iron should be removed previously by some other method[1].

[3] Schaeffer, J. Ind. Eng. Chem., 4:659 (1912).

[4] Am. J. Sci., (4) 2:416 (1897).

5. Indium chloride is soluble in a mixture of ether and strong hydrochloric acid saturated with hydrochloric acid gas, consequently the method of Gooch and Havens for the separation of aluminum and iron cannot be applied to indium and iron.

THE SECONDARY REACTIONS IN THE PREPARATION OF ZINC ETHYL

RUSH F. MCCLEARY[1] and ED. F. DEGERING

In 1849 in his research on free radicals, Frankland (1) treated zinc with ethyl iodide in a sealed tube at 150° C. As products of the reaction, he obtained a gas mixture, crystals of ethyl zinc iodide, and a clear liquid, zinc ethyl. His analysis of the gas gave 50.03 per cent butane, 25.79 per cent ethane, 21.7 per cent ethylene, and 2.48 per cent nitrogen. But neither Frankland nor subsequent workers have offered a satisfactory explanation of the mechanism of this reaction.

Various theories have been proposed to explain reactions of this type. Nef[2] proposed alkylidene dissociation, and produced experimental data for the Würtz reaction which indicated that sodium reacts with ethyl iodide to give 50 per cent butane, 25 per cent ethane, and 25 per cent ethylene. But alkylidene dissociation should also foster the formation of some butylene, and the relative quantities of the products formed if the alkylidene radical is the active intermediate in reactions of this type can be shown to be x mols of ethylene, y mols of butylene, $(x + 2y)$ mols of ethane, and z mols of butane. Expressed in equation form,

$2(x+2y+z)CH_2CH_2I + \text{dissociation} \rightarrow 2(x+2y+z)CH_3.CH\rightleftarrows^{3} + 2(x+2y+z)HI$

$2(x+2y+z)HI + 2(x+2y+z)Na \rightarrow 2(x+2y+z)NaI + 2(x+2y+z)H$

$xCH_3.CH\rightleftarrows + \text{rearrangement} \rightarrow xH_2C{:}CH_2$

$yCH_3.CH\rightleftarrows + yCH_3.CH\rightleftarrows \rightarrow yCH_3.CH{:}CH.CH_3$

$(x+2y)CH_3.CH\rightleftarrows + 2(x+2y)H \rightarrow (x+2y)CH_3.CH_3$

$2zCH_3.CH\rightleftarrows + 2zH \rightarrow zCH_3.CH_2.CH_2.CH_3$

However, these relationships are not satisfied by the data of either Frankland or Nef, which indicates either a faulty theory or faulty data.

Another theory that has been advanced to interpret reactions of this type is disproportionation. Experimental data seem to indicate that disproportionation reactions may involve either molecules or radicals or both, as illustrated by the following equations:

[1] Abstract of a thesis presented to the faculty of Purdue University by Rush Fox McCleary in partial fulfillment of the requirements for the degree of Master of Science.

[2] Data obtained from lecture notes of Dr. F. W. Upson, student of J. U. Nef.

[3] Free radicals are indicated by use of arrows.

$2HO_3S.CHBr.COOH$ + heat to M. P. (119.5°C) $\rightarrow HO_3S.CH_2.COOH + HO_3S.CBr_2.COOH$ (2)

$2CH_3.CH_2\rightarrow$ + diaproportionation $\rightarrow CH_3.CH_3 + H_2C{:}CH_2$ (3)

$CH_3.CH_3 + CH_3\rightarrow \rightarrow CH_4 + CH_3.CH_2\rightarrow$ (4)

To account for the thermal decomposition products of lead tetraethyl, Minert assumed the formation of ethyl radicals which he believed might react according to the following equations (5):

$CH_3.CH_2\rightarrow$ + H (from $PbET_4$) $\rightarrow CH_3.CH_3$

$2CH_3.CH_2\rightarrow$ (wall reaction or three body collision) $\rightarrow CH_3.CH_2.CH_2.CH_3$

$2CH_3.CH_2\rightarrow$ (wall reaction) $\rightarrow 2H_2C{:}CH_2 + H_2$

$2CH_3.CH_2\rightarrow$ + disproportionation $\rightarrow CH_3.CH_3 + H_2C{:}CH_2$

The work of Rice on the thermal decomposition of ethane is also of interest in this connection because alkyl radicals appear to be the active intermediates (6). He accounted for his products by the following formulation:

$CH_3.CH_3$ + thermal decomposition $\rightarrow 2CH_3\rightarrow$

$CH_3.CH_3 + CH_3\rightarrow \rightarrow CH_4 + CH_3.CH_2\rightarrow$

$CH_3.CH_2\rightarrow$ + loss of H $\rightarrow H_2C{:}CH_2 + H$

$CH_3.CH_3 + H \rightarrow H_2 + CH_3.CH_2\rightarrow \rightarrow H_2 + H_2C{:}CH_2 + H$

Doubtless either the alkylidene or alkyl radical is involved as an active intermediate in these secondary reactions in the preparation of zinc ethyl; hence it seemed advisable to make a quantitative study of the gaseous products of the reaction of zinc with ethyl iodide under controlled conditions, thus obtaining additional information on the mechanism of reactions of this type.

EXPERIMENTAL

Four hundred grams of powdered zinc and 60 grams of granular zinc were introduced into a one liter flask and activated by heating over a luminous flame for approximately two hours (7). During this heating the contents of the flask were stirred frequently to prevent caking. The flask was then attached to the apparatus as shown in Fig. I (flask *A*) and heated more strongly while the apparatus was being filled with carbon dioxide. The zinc was allowed to cool and 200 cc. of pure ethyl iodide were added through dropping funnel *B*. Then flask *A* was heated for 19 hours at 80°C by means of an oil bath equipped with a temperature regulator, and subsequently the temperature was raised and maintained at 105°C for four hours. The gases evolved were collected over water (previously saturated with the gases) and analyzed.

The type of apparatus devised for this research is quite suitable for the preparation, purification, and use of zinc ethyl as a reagent. The zinc ethyl iodide may be prepared as above, and then the zinc ethyl distilled off under reduced pressure and subjected to purification by fractional distillation by heating the initial receiver *C* with an oil bath. The first portion of the distillate is bypassed into receiver *D*. When the desired boiling point is reached, stopcocks *e* and *f* are closed and the pure zinc ethyl is collected in the graduated receiver *H*, from which any desired amount may be withdrawn into flask *E*. Here it can be diluted with a suitable solvent or introduced directly into reaction flask

G by the application of a slight vacuum. The other reagent can be added directly to flask *G* before the introduction of the zinc ethyl, or subsequently through separatory funnel *F*. If a reduced temperature is desired, flask *E* may be immersed in an ice or alcohol-carbon dioxide bath. Likewise flask *G* may be kept at the desired temperature. After a preparation, the entire apparatus is readily cleaned by distilling about 200 cc. of crude hydrochloric acid through the system, followed by a similar distillation with alcohol or acetone.

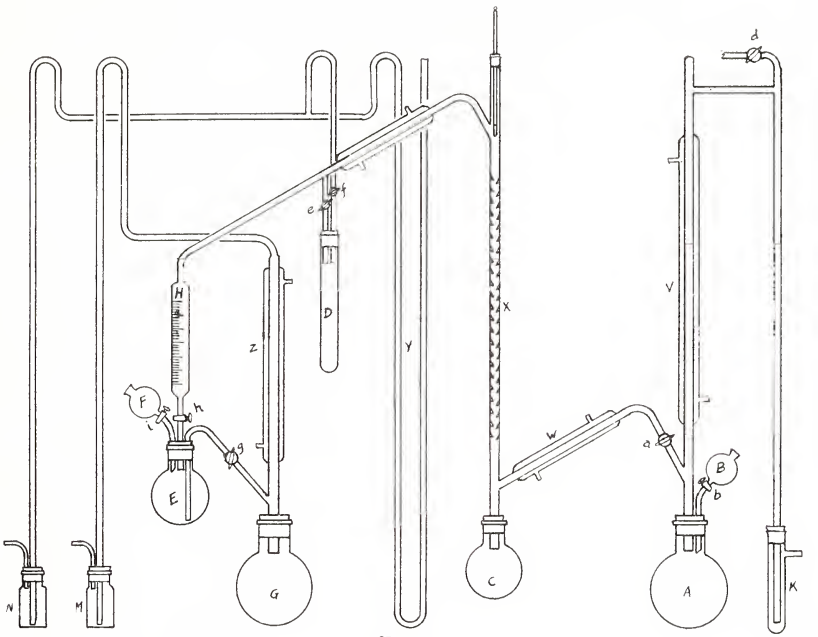


Fig I

In order to determine the effect of a higher temperature upon the amount and composition of the gases evolved, a series of runs was made in which the bath was heated to 90°C and maintained at this temperature for two hours. It was then heated to and maintained at 105°C for three hours. Subsequently it was allowed to rise slowly until it reached a maximum of 135°C at the end of ten and one-half hours.

The gases were freed of carbon dioxide by passage through a drying train, followed by an ascarite train, the hydrocarbons being collected over water, previously saturated with the gases. The gases were then bubbled through bromine at 0°C, the olefine constituents being absorbed without appreciable substitution. The volume of the olefines was determined by difference and the individual constituents identified by the physical properties of the resulting bromides. The residual saturated gases were measured and passed through a condenser coil immersed in an alcohol-carbon dioxide bath at —65°C to —70°C, where the butane was liquified. The liquified butane was then fractionated to remove any

dissolved ethane. Representative analyses of the ethane and butane fractions of the various runs, are respectively,

Analyses. Calc. for ethane fraction: C, 79.87; H, 20.13. Found: C, 79.97, 80.53, 80.16, 80.10, 80.00; H, 20.02, 19.47, 19.84, 19.90, 20.00. Calc. for the butane fraction: C, 82.65; H, 17.35. Found: C, 82.03, 82.42, 82.61, 82.20, 82.65; H, 17.97, 17.58, 17.39, 17.80, 17.34.

Should free hydrogen have been present the analytical separation would have placed it in the ethane fraction. In this event the ethane rather than the butane should have analyzed high in the percentage of hydrogen. However, the ethane fraction analyzed low in percentage of hydrogen, and the butane analyzed high in percentage of hydrogen. This was doubtless due to the difficulty in obtaining complete fractionation of the ethane from the butane.

The yield of zinc ethyl in each case was an inverse function of the volume of the gases evolved. The time required for the reaction to reach completion (8) and the temperature of the reaction are the chief factors in determining the volume of the gases evolved, the temperature being the more important variable.

At the lower initial temperature, the analysis of the gases evolved showed the following percentage composition for three separate determinations.

Volume of Gases Evolved with Temperature at 80°C for 19 hrs., then raised to and maintained at 105°C for four hours.				Volume of Gases Evolved with Temperature at 90°C for 2 hrs., then raised to 105°C for 3 hrs., and finally raised to 135°C.			
No.	% Butane	% Ethane	% Ethylene	No.	% Butane	% Ethane	% Ethylene
1	42.55	28.76	28.65	1	51.66	23.93	23.81
2	43.78	27.64	28.57	2	49.02	25.33	25.64
3	39.81	30.09	30.10	3	52.36	24.48	23.15

Whereas the amount of butane varied over a narrow range, the percentage of ethane and ethylene for a given run were in close agreement. In the bromine addition products there was no indication of the presence of butylene bromide, hence it seems that no butylene was formed in the reaction.

CORRELATION OF DATA

The above data are not in agreement with the theory of Nef, hence it seems that the alkylidene radical is not an intermediate in this reaction. However, if we assume the formation of free ethyl radicals, as Minert and other workers have done (9), the products obtained in the secondary reactions of zinc upon ethyl iodide may be accounted for by the following mechanisms:

(1) For the formation of butane, two ethyl-radicals may combine directly in a wall reaction or in a three body collision (10).

(2) For the formation of ethane and ethylene *in equi-molar quantities*, two ethyl radicals may react either by (a) a limited chain re-

action in a three body collision ($CH_3.CH_2\rightarrow$ $\rightarrow H_2C:CH_2 + H$; and $CH_3.CH_2\rightarrow + H\rightarrow CH_3.CH_3$), or (b) by disproportionation in a three body collision ($CH_3.CH_2\rightarrow + H.CH_2.CH_2 \rightarrow$ $\rightarrow CH_3.CH_3 + H_2C:CH_2$).

SUMMARY

1. An improved apparatus for the preparation, purification, and use of zinc ethyl as a reagent, is illustrated.

2. The data obtained indicate the mechanism of the secondary reactions of zinc upon ethyl iodide to be: (a) two ethyl radicals may combine directly in a wall reaction or in a three body collision to form butane, and (b) two ethyl radicals appear to react to form equi-molar quantities of ethane and ethylene. This appears to be a terniary collision involving a chain reaction or disproportionation.

3. The data indicate that the formation of gases is favored at higher initial temperatures, the formation of butane being especially so favored.

4. There was no indication of the formation of hydrogen nor of the formation of butylene, the only products of the reaction being butane, ethane, and ethylene.

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4. F. O. Rice, J.A.C.S., 53:1965 (1931).

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COLOR REACTIONS OF AMINO ACIDS WITH PHENOLS AND HYPOCHLORITES, INCLUDING NEW TESTS FOR TRYPTOPHANE AND PHENYLALANINE

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INTRODUCTION

In 1875 Engel[1] discovered what he thought to be a very delicate color reaction for glycocoll. This consisted in adding to its solution a few drops of phenol and a little sodium hypochlorite, which after standing a few minutes developed a beautiful blue color. Later investigators[2] found that other amino acids gave the color as well, and thought the reaction was based upon the splitting off of ammonia through the action of the hypochlorite. Proceeding on the above theory it was believed that fixed conditions might be established under which some of the amino acids could be made to react specifically. Such conditions were thought possible by varying the base of the hypochlorite, by using different phenols, or by using different degrees of alkalinity in the hypochlorite solutions.

EXPERIMENTAL

Preparation of Reagents: The amino acids, obtained from the Eastman Kodak Company, were made up in aqueous solution on the basis of their amino group rather than by their molecular weight. Best results were obtained when the hypochlorites were prepared by passing chlorine through a suspension or solution of the corresponding oxide or hydroxide. For purposes of comparison the alkalinity of all solutions was calculated as Na_2O and the hypochlorite as NaOCl. Phenol (C_6H_5OH) solutions were made up with water to 5 per cent by weight. The higher phenols were made up in alcoholic solution.

General Procedure: To 2cc. of the one-fiftieth molal (M/50) amino acid contained in a test tube were added 8 drops of the phenol and 2cc. of the hypochlorite solution. The contents were well mixed and the color observed immediately and at regular intervals thereafter.

The Use of Various Phenols: The list included phenol, o-, m-, and p-cresol, alpha and beta naphthol, guaiacol, hydroquinone, pyrocatechinol, and resorcinol. The colors obtained were usually brown or dark red and in no case did the use of the higher phenols show any advantage over phenol itself.

Alkali Concentrations in the Hypochlorite Solution: For this purpose known strength solutions of NH_4OH and of amino acids were made up. The alkalinity of the hypochlorite solutions was controlled by adding

[1] Henninger, A., Ber. Chem. Ges., 8:699 (1875).

[2] Zimmerman, W., Z. Physiol. Chem., 189:4 (1930); Furth, O., and Fromm, F., Biochem. Z., 220:69 (1930).

various amounts of standardized NaOH. The general procedure was followed. The results showed that the lower concentrations of free alkali gave the more satisfactory results.

A Study of Hypochlorite Concentrations: A series of sodium-, calcium-, barium-, and magnesium-hypochlorites were prepared in which the NaOCl content was controlled in the preparation. It was found that NaOCl concentrations above 2 per cent were undesirable, and that the most practicable results were obtained with solutions of below 1 per cent.

Reactions with Various Hypochlorites: When a solution of calcium hypochlorite was used upon one-fiftieth molal amino acids the following results were obtained in from 30 to 60 minutes:

(M/50) Amino Acids	NaOCl-0.95% Na_2O-0.03%	NaOCl-0.32% Na_2O-0.01%
Glycocoll	blue	
Alanine	blue	blue-green
Tyrosine	brown	yellow
Tryptophane	reddish-brown	rose
Leucine	blue	
Caprine	blue	
Proline	blue	
Phenylalanine	white turbidity	white turbidity
Histidine	pale brown	
Glutamic acid	blue	
Aspartic acid	yellow	

Using magnesium hypochlorite the following observations were made in from 30 to 60 minutes:

(M/50) Amino Acids	NaOCl-1.08% Na_2O-0.05%	NaOCl-0.27% Na_2O-0.013%	NaOCl-0.11% Na_2O-0.005%	NaOCl-0.04% Na_2O-0.001%
Glycocoll	blue			
Alanine	blue	pale blue		
Tyrosine	light brown			
Tryptophane	light brown	rose	rose	pink
Leucine	blue-green			
Proline	blue-green			
Caprine	blue-green			
Aspartic acid	yellow			
Asparagin	blue			
Phenylalanine	w. turbidity	w. turbidity		
Histidine	faint brown			
Glutamic acid	blue			

The immediate, specific color reaction of tryptophane should be noted. It is best shown when conditions are such that other amino acids fail to respond. The maximum color develops in from 30 to 60 minutes at room temperature, but can be speeded up by gentle heating.

The test for phenylalanine is no less specific but requires from 8 to 10 hours of standing at room temperature for the development of the white turbidity in the greater dilutions.

When sodium hypochlorite is used in the scheme outlined above similar results are obtained. Barium hypochlorite solutions react likewise but have a tendency to form precipitates.

The Deportments of Indole and Skatole: When indole and skatole are allowed to react under the same conditions as tryptophane, indole produces a white flocculent precipitate and skatole a white turbidity as compared with the rose color for tryptophane. By this means it is seen that indole and skatole may be differentiated and that their presence does not interfere with the specificity of the test for tryptophane.

The Deportment of Egg Albumin: A solution of egg albumin was prepared which contained as much tryptophane in the combined form as is present in a one one-hundredth molal solution of pure tryptophane. Aliquot portions of this solution were diluted with water in various proportions. The reagents were added as for the regular tryptophane test.

In a limited number of cases a faint greenish blue color developed, but in no case was there a trace of pink or rose. From this it was concluded that the test does not apply to tryptophane combined in the protein molecule.

The Deportment of Mixtures of Amino Acids: Mixtures of the amino acids previously studied were made up in the ratio in which they are found in egg albumin and in casein according to the best authorities.[3]

Observations based upon a large number of tests indicated that best results are obtained when very dilute solutions of sodium hypochlorite were used, the NaOCl content ranging between 0.13 and 0.022 per cent. Under these conditions the phenylalanine did not produce its turbidity and the tryptophane color remained clear in every case.

The Qualitative Detection of Tryptophane: A positive test is indicated by a beautiful rose or pink color which develops immediately and reaches a quite stable condition in from 30 to 60 minutes. Low concentrations of hypochlorite are essential and the free alkalinity must be maintained at a minimum. Concentrations of from 0.5 to 0.01 per cent NaOCl and from 0.5 to 0.002 per cent Na_2O in the hypochlorite solution work successfully. The test is especially specific at the lower concentrations of hypochlorite, because under such limitations all other amino acids fail to respond. Positive results have been obtained in solutions containing 0.0008 grams per cc.

The Qualitative Detection of Phenylalanine: A positive test is indicated by the development of a white turbidity which develops within 30 minutes with the higher concentrations of hypochlorite, but is considerably slower for the lower ones. Best results are obtained with

[3] The Biochemistry of the Amino Acids, A.C.S. Monograph No. 48, p. 191.

the more dilute solutions when allowed to stand from 8 to 10 hours. Concentrations of from 0.9 to 0.2 per cent NaOCl and from 0.25 to 0.003 per cent Na_2O work successfully.

The Quantitative Application to Tryptophane: The following amounts of reagents were added and in the order given: 2 cc. tryptophane, 4 cc. water, 8 drops phenol, and 2 cc. sodium hypochlorite. Color readings, using the Duboscq colorimeter, were taken at 30-minute intervals for 3 hours. A large number of samples were made up and 5 or more readings taken on each. Calculations showed that an average of 98.5 per cent of theory was obtained. The most suitable range was found to be between M/50 and M/150, and the time of standing from 2 to 3 hours. Gentle heating was found to accelerate the color equilibrium.

SUMMARY

The intensity of the blue color is given in no definite order by alanine, glutamic acid, carpine, asparagin, glycine, leucine, and proline. In general alanine gives the most intense color. Amino acids containing the benzene ring, such as tyrosine, tryptophane, and phenylalanine fail to give the blue color under ordinary conditions; histidine and aspartic acid likewise fail.

Among the various phenols C_6H_5OH is the most satisfactory. The reactions of the various hypochlorites are not specific.

A delicate test was worked out for phenylalanine, which is specific in that it produces a pronounced white turbidity with the more dilute solutions of hypochlorite.

Tryptophane yields a beautiful rose or pink at very low concentrations of hypochlorite. It can be detected in solutions containing 0.0008 grams per cc. Indole and skatole do not interfere. The test is not applicable to tryptophane when combined in the protein molecule but can be applied successfully when present in a mixture of amino acids. The characteristic color develops immediately and lends itself readily to quantitative applications.

A METHOD FOR AN OXIDIZING HYDROLYSIS OF OZONIDES PREPARED FROM UNSATURATED ACIDS

J. L. RIEBSOMER and RALPH C. TALLMAN,[1] DePauw University

Most vegetable fats and oils contain glycerides of unsaturated acids —some with only a small percentage, and others consist almost entirely of unsaturated materials. It is only the unsaturated acids with which this paper deals.

Ozone has been used since about 1900 for the determination of the structure of such acids. The general procedure has been to dissolve the acid in some solvent such as chloroform or acetic acid, pass ozone through the solution, and then to hydrolyze the resulting ozonide. This hydrolysis breaks the molecule into fragments at the positions of the unsaturated linkages.

Harries[2] did the pioneer work in this field. This investigator hydrolyzed the ozonide simply by boiling it with water. In working with an acid containing one double bond, this procedure would produce two aldehydes and two acids and necessitate the separation of four constituents, which might create quite a problem especially when small amounts are involved.

Noller and Adams[3] have hydrolyzed such ozonides under reducing conditions using zinc dust. This method produces two aldehydes from an unsaturated acid containing one multiple linkage. These investigators, however, were chiefly interested in the aldehyde ester for synthetic purposes. They found it possible to get yields as high as 60 to 70 per cent of fairly pure products. Upon repeated distillation of the aldehyde ester it was found that polymerization took place resulting in high boiling materials. Furthermore, the aldehyde groups readily oxidized to the corresponding acids upon standing in the air which resulted in a mixture of products. From an analytical standpoint these things are objectionable.

In our efforts to find a method of hydrolysis for ozonides which would give satisfactory yields and which would be as simple in application as possible, hydrogen peroxide was added to some ozonides in acetic acid solution and the hydrolysis carried out in this oxidizing medium. Hydrogen peroxide was given preference over dichromate and permanganate and other common oxidizing agents because it leaves nothing but water to remove from the mixture.

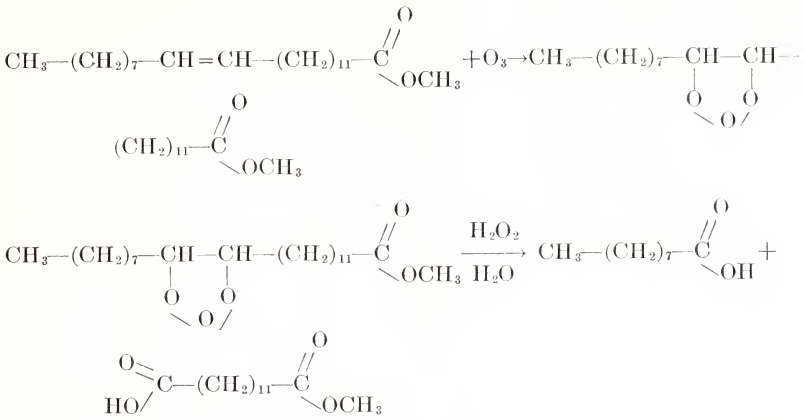
When this reaction was carried out, the fragments of the molecules were converted to the acids, the yields were as high as 62 per cent of the theoretical, and the separation of the products simplified.

This method was carried out using methyl erucate for which the reactions may be represented as follows:

[1] Dr. Tallman is an instructor of organic chemistry at Cornell University, Ithaca, New York. This work was carried out with him at that institution.

[2] Harries, Ber., 39:3732 (1906).

[3] Noller and Adams, J. Am. Chem. Soc., 48:1074 (1926).



This method has been used successfully in the study of the oil from Lycopodium spores[4], and in the investigation of pumpkin seed oil (Unpublished). Furthermore, the method applied to methyl oleate is being used as a laboratory exercise for students of organic chemistry. This procedure is not only of value for analytical purposes but may be used for the preparation of shorter chain fatty acids for which there is not always an adequate and inexpensive supply.

Experimental

Two hundred grams of erucic acid obtained from The Eastman Kodak Company was converted to the methyl ester by refluxing the acid with ten times the theoretical amount of methyl alcohol containing 4 cc. of concentrated sulphuric acid. After refluxing for five hours most of the excess methyl alcohol was distilled from the mixture over a steam bath. The ester was then washed, first with water to remove the sulphuric acid, then with a solution of 1 per cent sodium carbonate, and finally with a cold 1 per cent solution potassium hydroxide until all the unreacted acid had been removed. The ester was taken up in ether, dried with anhydrous magnesium sulphate and then distilled at 2.5 mm. pressure using an ordinary Claisen flask. At this pressure 198 grams of the ester boiled from 213-217°C. This represented 95 per cent of the theoretical yield.

Ninety-four grams of the methyl erucate thus prepared was dissolved in an approximately equal volume of dry acetic acid (note 1, at end of paper) placed in a round-bottomed flask with a ground glass joint and treated with ozone using the apparatus described by Henne[5]. Ozone was passed through until a small test sample did not decolorize a dilute solution of bromine in glacial acetic acid.

When this test indicated that ozone absorption was complete, the acetic acid solution of the ozonide was transferred to a 500 cc. flask connected with a condenser by means of a ground glass joint, note 2,

[4] Riebsomer and Johnson, J. Am. Chem. Soc., 3352 (1933).

[5] Henne, J. Am. Chem. Soc., 51:2676 (1929).

and 60 grams of hydrogen peroxide (30 per cent aqueous solution) was added. The mixture was heated over a steam bath for four to five hours, note 3, and finally over a low flame until all the peroxide was decomposed. The complete decomposition of the peroxide was indicated by adding a drop of the mixture to starch-iodide paper. When the test failed to give the usual blue color the reaction was completed.

This mixture contained water, acetic acid, pelargonic acid, and mono-methyl brassylate. To remove the water about 600 cc. of dry benzene was added, the whole placed in a round-bottomed flask to which was attached a Wurtz fractionating column. The flask was then heated in an oil bath which caused the benzene-water mixture to distill, note 4.

Acetic acid was removed from the mixture by transferring the dried liquid from above to a Claisen distilling flask, and distilling at a pressure of 40 mm. using an oil bath which was heated to a maximum of 110°C, note 5.

This procedure left in the distilling flask a small quantity of acetic acid, pelargonic acid, and mono-methyl brassylate. In order to convert the acid ester to the methyl esters, this mixtures was treated with methyl alcohol according to the procedure indicated above for the conversion of erucic acid to the methyl ester.

After drying the esters so produced, the mixture was fractionally distilled using a modified Claisen flask, with the following results:

Fraction	Pressure (mm.)	Temperature °C.	Grams Distillate
1	3.5	69-72	28.5
2	3.5	72-160	3.5
3	3.5	160-162.5	45.0
4	3.0	161-190	8.0
Residue			

Fraction 1 proved to be methyl pelargonate and fraction 3 was dimethyl brassylate. The weights indicated above represent slightly better than 62 per cent of the theoretical yield of each of the products.

NOTES ON PROCEDURE

1. The dry acetic acid was prepared by adding excess acetic anhydride to ordinary glacial acetic acid and refluxing for two to three hours.

2. An ordinary flask and condenser may be used if the stopper is well wrapped with tin foil.

3. When heating of the ozonide and hydrogen peroxide mixture is started, care must be used to prevent the reaction from becoming too vigorous.

4. If the water was not all removed by the first distillation, more benzene was added and the process repeated.

5. Pelargonic acid distills at 110°C at a pressure of two millimeters; little was lost by this procedure.

SUMMARY

1. A detailed procedure for the oxidizing hydrolysis of unsaturated fatty acid ozonides has been presented.

2. This method has been used successfully in the solution of problems involving the determination of structure of naturally occurring unsaturated acids.

3. The procedure is simple in practice. It has been used successfully in the hands of elementary organic chemistry students.

SOME EXPERIMENTS IN COLORING CELLOPHANE

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As is well known cellophane may be easily and attractively colored by many organic dyes, all the direct cotton dyes being taken up very readily. Mention in the literature of any attempts to use inorganic substances for a similar purpose seem to be lacking.

The experiments here described were undertaken at the suggestion of Mr. R. B. Withrow of the Horticultural Department of Purdue University who was carrying on an investigation to determine the effect of artificial light on plant growth. Colored cellophane had been used to modify the quality of the light. As the organic dyes do not absorb the extreme red end of the spectrum satisfactorily, the thought occurred that inorganic colors might serve better. Mr. Withrow had used cellophane screens colored with Prussian blue in some of his work, the results of which are soon to be published. His preliminary experiments with Prussian blue showed that cellophane could be colored with inorganic substances, the desired colored substance being formed directly in the cellophane.

The cellophane used in these experiments was Dupont's number 600, which is about twice as heavy as that used for ordinary commercial wrappings. The preliminary experiments with Prussian blue seemed to indicate that the colored compound was formed in the cellophane in a colloidal condition and was not deposited on the surface. This led to the belief that those substances which easily entered into the colloidal state might give the most satisfactory results.

The general method of procedure was to soak the cellophane in water until free from glycerine. The wet cellophane was then placed for a few minutes in a dilute solution, usually 1 or 2 per cent of one of the reacting substances. On removal from this solution the excess of reagent was washed from the surface with running water, the cellophane immediately immersed in a solution of the necessary reagent to produce the desired compound and left as long as the color continued to develop. Finally it was washed in running water. If the color was not as intense as desired the process was repeated until the desired intensity was obtained.

Prussian blue, the first color used, was obtained by immersing first in ferric chloride solution and then in potassium ferrocyanide solution. The color developed well and the intensity was easily controlled by repeating the process the desired number of times, or if desired, increasing the concentration. The color so produced was perfectly fast to water. It seemed to make some difference in which of the solutions the cellophane was placed first though no specific experiments have been made to determine this point.

Turnbull's blue was produced by treating the cellophane successively with solutions of ferrous sulfate and potassium ferricyanide. This also gave a very satisfactory blue which was fast to water.

A very good yellow can be obtained with cadmium sulfide. The cellophane is first put into a dilute solution of cadmium sulfate and after washing transferred to a solution of sodium sulfide. The color developed easily and evenly to give a clear yellow. The color from antimony sulfide was not so satisfactory, was more difficult to obtain in the desired intensity and was not taken up quite so evenly. Good greens were produced by coloring first with cadmium sulfide and then with one of the blues until the desired shade of green was obtained.

Orange reds were obtained by immersing first in dilute ferric chloride solution and after washing transferring to boiling water. The desired intensity could be obtained by repeating the process a sufficient number of times. Concentration of the ferric chloride solution was also a factor. The color is fast to water and light.

With 1 per cent solutions of uranyl nitrate and potassium ferrocyanide a good, clear red brown (burnt orange) was easily obtained. This color was fast to water and sunlight.

Potassium permanganate in solution is easily reduced by cellophane, slowly at room temperatures, rapidly at the boiling point. At the same time the cellophane itself is colored by the reduction products of the permanganate. The color may vary from a light straw color, if the solution is dilute and the time of exposure short, to a dark brown, if the concentration is greater and the exposure longer. With long exposure the cellophane becomes brittle and cracks. The light browns fade on long exposure to direct sunlight.

Colloidal gold and silver can also be deposited in the cellophane by the use of proper reducing agents. With tannin as the reducing agent and very dilute solutions of gold chloride and silver nitrate, gold gives a good purple and silver a golden brown. Other reducing agents have not as yet been tried. Cellophane itself will reduce gold chloride, but some of the gold is deposited on the surface and is not colloidal. In the case of the silver, at least, it proved best to treat the cellophane with the tannin solution first.

Lead acetate and potassium chromate easily produced a good yellow but gave to the cellophane a translucent or almost opaque appearance.

In attempting to test the fastness of these colors to sunlight eight small samples of cellophane with inorganic colors and three with organic were clamped in a frame so that half the sample was covered and half exposed. These were placed in direct sunlight from three to six hours a day for a period of three months. All the organic colors faded more

or less though the red showed only slight fading. Of the inorganic substances ferric hydroxide, the uranyl compound, cadmium sulfide, and colloidal gold were unaffected and Prussian blue very slightly affected. The other three showed more or less definite fading.

The accompanying table gives a summary of the results.

Dye Reacting substances	Color	Condition of Color	Fastness to Sunlight
$FeCl_3+K_4Fe(CN)_6$	Bright blue	Even, transparent good	Almost fast
$FeSO_4+K_3Fe(CN)_6$	Bright blue	Even, transparent good	Fades slightly
$CdSO_4+Na_2S$	Bright yellow	Even, transparent good	Fast
$K(SbO)C_4H_4O_6+H_2S$	Orange yellow	Difficult to form, fair, somewhat uneven	.....
$UO_2(NO_3)_2+K_4Fe(CN)_6$	Burnt orange	Good, even, transparent	Fast
$FeCl_3$+hot water	Orange	Good, even, transparent	Fast
$KMnO_4$	Brown	Even, transparent	Fades badly
$AuCl_3$+tannin	Purple	Good, even, transparent	Fast
$AgNO_3$+tannin	Golden brown	Good, even, transparent	.....
$CuSO_4+K_4Fe(CN)_6$	Red brown	Uneven	.....
$CoCl_2+K_3Fe(CN)_6$	Light purplish brown	Fair, even, transparent	.....
$K_2Cr_2O_7+SO_2$	Very light green	Very slow in developing	.....
$CuCl_2+NaOH$	Light green	Slow in forming, too light	Fades to yellow
$Pb(C_2H_3O_2)_2+K_2Cr_2O_4$	Yellow	Translucent to opaque, forms easily	.....
$NiCl_2$+Dimethyl glyoxime	Pink	Somewhat cloudy	.....
Carbic violet 16175	Violet	Good	Fades noticeably
Pontamine fast red 8 B.L.	Deep scarlet	Very good	Fades slightly
Orange G	Orange	Good	Fades badly

THE DISSOCIATION CONSTANTS OF MONO- AND TRICHLOROACETIC ACIDS IN ETHYL ALCOHOL

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The purpose of this investigation was to determine the success with which the dissociation constants of organic acids in alcoholic solutions can be determined by electromotive force measurements of cells without liquid junction potentials and with easily reproducible electrodes such as the hydrogen and silver-silver chloride electrodes. The electromotive forces of cells of the type

$$Ag/AgX/HX(m_0),\ MX(m)/H_2/HX(m_1)/AgX/Ag$$

have proved very useful in determining the activity coefficients of some strong acids and hydroxides in aqueous salt solutions. Harned and Robinson[1] have measured the electromotive forces of cells of the type

$$Ag/AgX/HX(m_0),\ MX(m_3)/H_2/HAc(m_1),\ MX(m_2)/AgX/Ag$$

for solutions of a weak acid (HAc) in aqueous solutions of salts (MX). From these values they have determined the ionic concentrations and the activity coefficients of weak acids, such as acetic, in potassium, sodium, lithium, and barium chloride solutions. Harned and Fleysher[2] have measured the activity coefficient of hydrochloric acid in ethyl alcohol solutions by means of the hydrogen and silver-silver chloride electrodes. Harned and Owen[3] have investigated the thermodynamic properties of weak acids and bases in aqueous salt solutions and have developed an exact method for the determination of their dissociation constants from cell measurements. The question naturally arises as to whether or not measurements with the same type of cell can be extended to alcoholic solutions of weak and moderately strong organic acids.

The limitations of the method depend upon experimental accuracy, upon the difficulty of obtaining a reversible electromotive force of the hydrogen electrode when the ratio of the molality of the hydrogen ion to that of the dissolved salt is very small, and upon the successful application of the Debye-Hückel equation in determining the activity coefficient of an electrolyte in solutions of the type considered.

Let us consider in alcoholic solution the cells,

$$H_2/HAc(M),\ LiCl(m)/AgCl/Ag,$$

which has an electromotive force equal to E, and

$$H_2/HCl(0.01)/AgCl/Ag,$$

with an electromotive force equal to 0.2109. This value has been taken from the results of Harned and Fleysher. HAc is used to represent any weak acid. Then the electromotive force of the cell

[1] Harned and Robinson, J. Amer. Chem. Soc., 50:3157 (1928).
[2] Harned and Fleysher, ibid., 47:82 (1925).
[3] Harned and Owen, ibid., 52:5079 (1930).

$$H_2/HAc(M),\ LiCl(m)/AgCl/Ag/AgCl/HCl(0.01)/H_2$$

is given, according to the Nernst equation, as follows:

$$E-0.2109=\frac{RT}{F}\ln\frac{(0.563)^2(0.01)^2}{\gamma_H\gamma_{Cl}{}^m\ m_H} \tag{1}$$

or in another form as

$$16.9062\ E + 0.9332 + \log m + 2\log\gamma = -\log m_H, \tag{2}$$

in which 0.563 has been taken from the results of Harned and Fleysher as the activity coefficient of 0.01 molal hydrochloric acid in ethyl alcohol. The term, log m, refers to the logarithm of the molality of the added salt. The term, log γ, represents the logatrithm of the activity coefficient of hydrochloric acid in a solution of a weak acid the molality of which is M-m_H:

$$\gamma=\sqrt{\gamma_H\gamma_{Cl}} \tag{2}$$

The value of log γ can be determined by an application of the equation of Debye and Hückel[4] which has been proved valid for the low concentration of acid and salt employed. This equation is

$$-\log\gamma=\frac{A\sqrt{2\mu}}{1+\alpha\sqrt{2\mu}}-2B\mu, \tag{3}$$

where A, B and α are constants which are used here in the same sense as they have been defined by Hückel. Scatchard[5] has determined the values of these constants for lithium chloride solutions in pure ethyl alcohol as follows:

$$A = 1.973;\ \alpha = 2.36;\ B = 0.025.$$

It is assumed that the presence of the undissociated molecules of the weak acid will have no greater effect on the activity coefficient of the hydrogen ion than the molecules of the solvent. The error introduced by this assumption is recognized as one worthy of consideration in solutions containing the concentration of acid which we have employed. It is believed, however, that this error is small and in any event is unavoidable.

Since the sum of the concentrations of the dissolved salt and the hydrogen ion resulting from the dissociation of the weak acid is unknown, the ionic strength of the dissolved salt alone is used as the total ionic strength in equation (3). We are justified in doing this since it has been shown by Harned and Robinson that at concentrations of HCl up to 0.01 molal in salt solutions the activity coefficient of the hydrogen ion is independent of the concentration of the acid but dependent upon the total ionic strength. This may be readily understood, since the activity of the ion depends upon the atmosphere of ions surrounding it and not upon the proximity of any particular kind of ion. Accord-

[4] Hückel, Physik. Z., 26:93 (1925).

[5] Scatchard, J. Amer. Chem. Soc., 47:2098 (1925).

ingly, since the concentration of the hydrogen ion produced by the ionization of a weak acid is very small when compared to the concentration of the ions produced by the ionization of a salt, we may use the molality of the salt as a first approximation without introducing any great error. In the case of univalent salts the ionic strength is numerically equal to the concentration. By using the ionic strength of the dissolved salt an approximate value of log γ is obtained. This value is then substituted in equation (2), and an approximate concentration of the hydrogen ion is obtained. This concentration of the hydrogen ion may now be added to the concentration of the dissolved salt to obtain a more accurate value of the total ionic strength. Thus, by the method of successive approximations, an exact value of m_H is obtained.

The thermodynamic expression for the dissociation constant of an electrolyte is:

$$K=\frac{\gamma^2}{\gamma\mu}\cdot\frac{m_H{}^2}{M-m_H}=\frac{\gamma^2}{\gamma\mu}k, \tag{4}$$

in which $\frac{\gamma^2}{\gamma\mu}$ is substituted for the more complete expression $\frac{\gamma_H\,\gamma_{Ac}}{\gamma_{HAc}}$.

HAc again represents any weak acid. This equation is valid when γ is equal to unity at infinite dilution of the electrolyte in any solvent. The activity coefficient has been defined as equal to unity at infinite dilution by the equation of Debye and Hückel. Thus, the value of k approaches K as the concentration of the electrolyte approaches zero. But it is not equal to K at any other concentration. The term, k, is defined by the following equation:

$$k=\frac{m_H{}^2}{M-m_H} \tag{5}$$

and can be easily calculated for any given concentration of the electrolyte by measuring the molality of the hydrogen ion by the method outlined above. The value of k as so determined refers to a solution containing a dissolved salt and is not the same as it would be if the acid were in a solution to which no salt had been added. Furthermore, it is impossible to extrapolate to infinite dilution the curve obtained by plotting the values of k against the molality of the dissolved salt, since the slope of the curve becomes very great as the molality becomes very small.

In order to determine the value of k in salt free solutions the following method was used. This is essentially the same method as Harned and Owen (loc. cit.) used for a similar purpose. Let us assume that the activity coefficient of the undissociated acid is unity. The basis for this assumption will be given later. Equation (4) then becomes

$$K=\gamma^2 k. \tag{6}$$

By taking the logarithm of equation (6) we obtain

$$\log K=2\log\gamma+\log k. \tag{7}$$

According to the Debye-Hückel equation,

$$\log\gamma = -\frac{A\sqrt{2\mu}}{1+\alpha\sqrt{2\mu}}2B\mu. \tag{8}$$

Substituting the value of $\log\gamma$ in equation (7) we obtain

$$\log K = -\frac{2A\sqrt{2\mu}}{1+\alpha\sqrt{2\mu}}+4B\mu+\log K. \tag{9}$$

Transposing equation (9),

$$\log k - \frac{2A\sqrt{2\mu}}{1+\alpha\sqrt{2\mu}} = \log K - 4B\mu. \tag{10}$$

Let us now define two new terms:

$$S = \frac{2A\sqrt{2\mu}}{1+\alpha\sqrt{2\mu}}, \tag{11}$$

and

$$N = \log k - S. \tag{12}$$

Substituting these terms in equation (10) we obtain

$$N = \log K - 4B\mu. \tag{13}$$

Let us write the following equation

$$2\log m_H = N+S+\log(M-m_H), \tag{14}$$

which is obtained from equations 5 and 12:

$$2\log m_H = \log k+\log(M-m_H)$$
$$\log k = N+S.$$

The ionic strength is now plotted against N, and extrapolation is made to zero concentration of the dissolved salt. The value of N is read from the plot. An approximate value of m_H in a salt free solution is obtained by taking the molality of the hydrogen ion in the solution containing the smallest concentration of lithium chloride. This value is then substituted in the right hand member of equation 14, and a new molality of the hydrogen ion is determined. This more accurate value of m_H is in turn substituted in the right hand member of the equation, and the equation is solved again. This process may be repeated until the equation is satisfied, at which time the value of m_H obtained is the exact value which it would have in a salt-free solution.

Let us now return to the expression for the dissociation constant of an electrolyte, equation 4. It is now possible to determine m_H and $M - m_H$ from measurements of the cells of the type already discussed, and γ can be evaluated by means of the Debye-Hückel equation. But $\gamma\mu$ cannot be determined directly unless K is known or vice versa. Nevertheless, K can be readily evaluated if we supplement the data with certain assumptions which are supported by a large number of experimental facts and which lead to an indirect evaluation of $\gamma\mu$.

The value of $\gamma\mu$ is found by assuming that in very dilute solutions the activity coefficient of the undissociated electrolyte is equal to unity, and that the activity, therefore, is equal to the concentration. This assumption is warranted by the success of the interionic attraction theory in explaining the activity changes of strong electrolytes in solutions of varying concentrations. If the change in the activity coefficient of an ion depends entirely upon the interionic forces, as the evidence tends to show, there is no reason to expect that the activity coefficient of a neutral molecule will vary appreciably in dilute solutions. Aside from this theoretical reasoning, there is good experimental evidence upon which to base the above assumption. Very few activity measurements have been made in solutions of non-electrolytes, but those which have been made show that the changes are very small. In aqueous glycerine solutions the activity coefficient of glycerine changes from 1 at zero concentration to 1.006 in a 0.1 molal solution.[6] Randall and Failey[7] have reviewed the work relating to the activities of neutral substances, such as gases and non-electrolytes, dissolved in salt solutions. They have shown that the quotient of the logarithm of the activity coefficient of gases and non-electrolytes and the ionic strength of the dissolved salt in aqueous salt solutions is approximately a constant. This constant varies with the salt and non-electrolyte used.

If the quotient of the logarithm of the activity coefficient of the undissociated part of the weak acid and the ionic strength of the added salt is approximately constant, it follows that

$$\log\gamma_\mu = C\mu,$$

As μ becomes zero, $\log \gamma\mu$ becomes equal to zero, or $\gamma\mu$ equal unity.

Hence, the expression $\frac{\gamma^2}{\gamma\mu}$ is equal to γ^2 only at infinite dilution of the added salt. Since we are concerned only with the dissociation constant in salt-free solutions, we may write equation 4 in the following form:

$$K = \gamma^2 \frac{m_H{}^2}{M - m_H} \qquad (15)$$

upon the basis of the simple assumption that the dissociated part of weak acids behaves in the presence of added salts in the same manner as the ions of HCl.

PREPARATION OF MATERIALS

Ethyl Alcohol. Absolute ethyl alcohol was the solvent used. This was prepared by treating 95 per cent alcohol three times with quicklime which had been freshly prepared by heating hydrated lime at a temperature of 600-700° C. in an electric furnace. One liter of alcohol was treated with 300 grams of this lime and refluxed for twelve hours. The alcohol was distilled, and the treatment was twice repeated. When needed for the preparation of solutions, the alcohol was distilled from the last portion of the lime, heated with basic lead acetate to remove

[6] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw Hill Book Company, Inc., New York, 1923, p. 288.

[7] Randall and Failey, Chem. Revs., 4:271 (1927).

aldehydes, and finally distilled through a sixteen-bulb Young's fractionating column into a dry flask. The alcohol thus prepared was used at once. The usual precautions were taken to protect the alcohol from contact with moist air and corks. The water content of the alcohol was checked by means of tests with a xylene solution of aluminum ethylate.[8] The refractive index of each sample was also determined by means of a pulfrich refractometer. There is considerable variation in the refractive index of the alcohol produced by this method. The alcohol used possessed a refractive index N_D^{20} of 1.3592 (0.0006). Schiff's reagent was used to detect aldehydes. Such tests were negative, or very slightly positive after standing for a few minutes.

Hydrogen. The supply of hydrogen for the hydrogen electrode was obtained by the electrolysis of a solution of sodium hydroxide. The gas was purified by passage through tubes filled with glass-wool, calcium chloride, and platinized asbestos heated to 300° C. It was finally dried by passage through a long tube filled with calcium chloride. To prevent any change in the composition of the solution in the cell the hydrogen was passed through an efficient saturating system consisting of three or more containers which were filled with solutions of the same composition as that in the cell. A trap was fixed at the end of the hydrogen outlet of the cell for the purpose of preventing the entrance of moisture and air. This trap was filled with a solution of the same composition as that in the cell.

Lithium Chloride. The lithium chloride was obtained from Coleman and Bell and was of the highest purity. This was fused and cooled in a dessicator prior to use.

Acids. Monochloroacetic acid (Baker) and trichloroacetic acid (Eastman), of the highest purity obtainable, were dried for six days prior to use in a dessicator over P_2O_5.

Silver. The silver used in the preparation of the silver-silver chloride electrode was deposited by a current of five to seven amperes in a cell consisting of an anode of pure silver and a cathode of platinum wire immersed in a solution of silver nitrate. The silver deposited by the use of this large current was crystalline and could be dislodged easily from the platinum wire by gentle tapping. The silver was washed many times by decantation with conductivity water and was kept in conductivity water until ready for use.

Silver Chloride. The silver chloride was prepared by adding a solution of pure hydrochloric acid to a dilute solution of silver nitrate which was acidified with nitric acid. The silver chloride was washed many times with a dilute solution of nitric acid in conductivity water, followed by washing with conductivity water alone, and finally placed in water until required for the preparation of the electrodes. Since silver chloride is sensitive to light, the precipitation and subsequent treatment were carried out in brown bottles or in a dark-room. During use, the electrode-vessel was placed in the darkened air bath.

[8] Henle, Ber., 53:719 (1920).

APPARATUS

Potentiometer. A Leeds and Northrup Type K Potentiometer was used with a Leeds and Northrup Type R reflecting galvanometer to measure the electromotive forces of the cells. Two Eppley Standard Cells were connected by a switch so that either cell could be used as a reference or serve as a check against the other. The calibrations of these cells were certified by the manufacturer.

Cell. The cell consisted of a hydrogen electrode and a silver-silver chloride electrode. These electrodes were immersed in the solution which was contained in a glass cylinder 4 centimeters in diameter and 12 centimeters in height. The hydrogen electrode, the silver-silver chloride electrode, the inlet, and the outlet for hydrogen were mounted in a rubber stopper. The cell was placed in an air bath within which the temperature was maintained at 25° C. ($\pm 1°$).

Hydrogen Electrode. The electrodes consisted of platinum foil, 5-15 millimeters. The foil was fused to platinum wire, which was sealed into a glass tube. Contact was made by filling the tube with mercury. The method of preparing the platinized electrodes (black) was that suggested by Popoff, Kunz, and Snow.[9] The bright platinized electrodes were prepared according to the method of Kolthoff and Kameda.[10]

A short length of platinum wire was first cleaned by means of a solution of potassium dichromate and concentrated sulphuric acid. The wire was then washed in distilled water and heated to dull redness. The plating bath contained a solution of chloroplatinic acid the concentration of which corresponded to 2 per cent platinum. By electrolysing for two minutes at a current strength of twenty milliamperes, the electrodes were covered with bright platinum. After plating, the electrodes were washed for thirty minutes in conductivity water through which hydrogen was passing. Finally, they were washed with the solution to be studied, which was also saturated with hydrogen. These electrodes gave reproducible results.

Silver-silver Chloride Electrode. In this work the old type of electrode, which consists of silver covered with a layer of silver chloride, was replaced by finely divided silver over which a layer of silver chloride was placed. This type of electrode provides intimate contact of silver and silver chloride. The potential of this electrode does not vary as the potential has been found to do when one uses an electrode in which the silver has not crystallized freely and in which there is more or less internal strain. To prepare the electrode the required amounts of silver and silver chloride were washed separately many times by decantation with the solution to be used in the cell. The silver was then placed in the bottom of a small cup to which was sealed a bent tube. Contact was made with silver by means of a platinum wire fused in the seal and with the circuit by means of mercury placed in the tube. This tube was mounted in the rubber stopper of the cell as already described. The layer of silver chloride was then placed upon top of the silver in the cup. This electrode has been suggested by Linhart.[11]

[9] Popoff, Kunz, and Snow, J. Phys. Chem., 32:1056 (1928).

[10] Kolthoff and Kameda, J. Amer. Chem. Soc., 53:821 (1931).

[11] Linhart, J. Amer. Chem. Soc., 41:1175 (1919).

The constant temperature air bath, the potentiometer, and the galvanometer were carefully shielded to minimize the errors of variable measurements due to induction. All wiring was of solid construction.

EXPERIMENTAL RESULTS

The Dissociation Constant of Monochloroacetic Acid. The results obtained with the usual types of platinum black electrodes can be characterized as unreliable in unbuffered solutions of the type under investigation. The electromotive forces of the cells change rapidly up and down over wide ranges. Two electrodes in the same solution fail to give the same result. Even the direction of the drift of the electromotive force varies. As a general rule the electromotive force increases for a time, passes through a maximum, and finally decreases indefinitely. In some instances, when the deposit of platinum black is very light, equilibrium is reached after about five hours. The adsorption of the cation of the salt on the surface of the platinum black in a hydrogen atmosphere and the gradual release of the cation, resulting in decreasing acidity of the solution, is generally thought to be the cause of the fluctuation of potential. In the solutions used in this investigation it is possible that hydrochloric acid is liberated by the action of hydrogen upon the chloroacetic acids. This action cannot be the sole cause, however, of the variations since the drift is not always in the same direction.

The electromotive forces of cells containing monochloroacetic acid solutions were determined by the use of electrodes which were coated with very slight deposits of platinum black. In these solutions, a fair state of equilibrium was attained and fairly reproducible results were obtained. The dissociation constant of monochloroacetic acid, as reported, has been determined from measurements made with the electrodes prepared in accordance with the directions of Popoff, Kunz, and Snow. The electromotive force determinations and the values of the function employed in the calculation of the dissociation constant are given in Tables I and II.

TABLE I

Electromotive Force Measurements
(0.20 m Monochloroacetic Acid)

m LiCl	E. M. F.	$\log\gamma$	S
0.0000	.....	—0.04933	0.09902
0.0500	0.2720	—0.35480	0.71460
0.0562	0.2737	—0.36648	0.73858
0.0839	0.2828	—0.40830	0.82498
0.0858	0.2815	—0.40901	0.82660
0.0895	0.2892	—0.41330	0.83556
0.1040	0.2928	—0.42910	0.86872
0.1297	0.2972	—0.45863	0.93022
0.1311	0.3013	—0.46981	0.94272

TABLE II

Molality of the Hydrogen Ion and Extrapolation Function
(0.20 m Monochloroacetic Acid)

m LiCl	log m_H	m_H	N
0.0000	—3.44433	0.000359	(—6.28200)*
0.0500	—3.52106	0.000301	—7.05710
0.0562	—3.57724	0.000265	—7.19353
0.0839	—3.82143	0.000151	—7.76982
0.0858	—3.80202	0.000158	—7.73132
0.0895	—3.94794	0.000113	—8.03223
0.1040	—4.03942	0.000095	—8.24839
0.1297	—4.14340	0.000070	—8.53783
0.1311	—4.20024	0.000063	—8.65411

*By extrapolation

Reproducible results cannot be obtained when the ratio of the molality of the lithium chloride to the molality of acid is very large or very small. To obtain reproducible results in dilute solutions of lithium chloride it is necessary to measure the electromotive force of water-alcohol mixtures in which the molalities of lithium chloride and monochloroacetic acid are constant. Extrapolation can then be made to find the value of the electromotive force when the solvent is absolute alcohol. When the logarithm of the electromotive force is plotted against the per cent of alcohol (by weight), a straight line is obtained. This permits an accurate extrapolation. In order to determine the validity of this extrapolation, the electromotive force of a solution in 100 per cent ethyl alcohol as the solvent was determined for a molality of lithium chloride which gives reproducible results. The electromotive force of the same solution was then calculated by the method of extrapolation. The results (Table III) were in good agreement.

TABLE III

Extrapolation of E. M. F. to Absolute Ethyl Alcohol
(0.20 m Monochloroacetic Acid; 0.1297 m Lithium Chloride)

% Ethyl Alcohol	E. M. F.	log E
80	0.3603	—0.44334
85	0.3445	—0.46281
90	0.3265	—0.48612
95	0.3120	—0.50585
100 (measured)	0.3007	—0.52187
100 (extrapolated)	0.2972	—0.52700

The dissociation constant of the acid is obtained by substituting the value of N obtained by extrapolating to zero molality of lithium chloride in equation 14 and calculating the molality of the hydrogen ion in the manner described. The molality of the hydrogen ion resulting

from the dissociation of 0.20 molal monochloroacetic acid in a salt-free solution in ethyl alcohol was found to be 0.0003595. The activity of the hydrogen ion is determined by multiplying the molality of the hydrogen ion by its activity coefficient calculated at that molality by means of the Debye-Hückel equation. The ionic strength is equal to the molality of the hydrogen ion. The value of K was next obtained by means of the usual thermodynamic equation. For monochloroacetic acid in ethyl alcohol K was found to be 5.224×10^{-7}. This value appears to be much higher than the expected value, although the only determination with which it can be compared is that of Godlewski (loc. cit.) who obtained 1.20×10^{-7}.

The dissociation constant of monochloroacetic acid was also determined from electromotive force measurements made by using bright platinum electrodes. The results of these measurements are given in Tables IV and V.

TABLE IV

Electromotive Force Measurements
(0.20 m Monochloroacetic Acid)

m LiCl	E. M. F.	log γ	S
0.0000	.....	—0.06773	0.10480
0.0350	0.2729	—0.31830	0.64360
0.0496	0.2800	—0.34635	0.69770
0.0752	0.2841	—0.39621	0.80014
0.1200	0.3017	—0.44291	0.89782

TABLE V

Molality of the Hydrogen Ion and Extrapolation Function
(0.20 m Monochloroacetic Acid)

m LiCl	log m_H	m_H	N
0.0000	—3.41852	0.0003815	—6.24200
0.0350	—3.45437	0.0003513	—6.85363
0.0496	—3.66971	0.0002139	—7.33870
0.0752	—3.82017	0.0001513	—7.74218
0.1200	—4.22716	0.0000593	—8.65404

The dissociation constant of monochloroacetic acid as calculated from these values is 5.220×10^{-7}. The molality of the hydrogen ion decreases with increasing molality of lithium chloride.

The Dissociation Constant of Trichloroacetic Acid. The bright platinum electrodes were used in this determination. The results obtained were very satisfactorily reproducible when the ratio of the molality of lithium chloride to that of the acid was very small. These results are reported in Tables VI and VII.

TABLE VI

Electromotive Force Measurements
(0.10 m Trichloroacetic Acid)

m LiCl	E. M. F.	log γ	S
0.0000	.....	—0.06430	0.12922
0.0350	0.2389	—0.31830	0.64360
0.0496	0.2273	—0.34635	0.69770
0.0752	0.2206	—0.39621	0.80014
0.1000	0.2135	—0.42490	0.85980
0.1200	0.2088	—0.44291	0.89782

TABLE VII

Molality of the Hydrogen Ion and Extrapolation Function
(0.10 m Trichloroacetic Acid)

m LiCl	log m_H	m_H	N
0.0000	—3.21406	0.00061	(—5.49000)*
0.0350	—2.88056	0.00132	—5.40904
0.0496	—2.84978	0.00141	—5.39109
0.0752	—2.74562	0.00179	—5.28534
0.1000	—2.69287	0.00202	—5.23668
0.1200	—2.65826	0.00219	—5.20468

*By extrapolation.

The dissociation constant of trichloroacetic acid calculated from the above data is 3.236×10^{-6}. Goldschmidt[12] obtained 1.48×10^{-6}. Larsson[13] has corrected Goldschmidt's value and obtained 1.01×10^{-6}. Larsson also determined the dissociation constant of trichloroacetic acid by potentiometric methods and found K to be 2.09×10^{-6}. The value 4.54×10^{-6} is quoted by Walden.[14]

For the solutions of trichloroacetic acids, the molality of the hydrogen ion appears to increase with increasing molality of lithium chloride. This is contrary to the effect of lithium chloride in the solutions of monochloroacetic acid. It will be noted, however, that the molalities of the hydrogen ion as determined in the trichloroacetic acid solutions are much larger than those of the monochloroacetic acid solutions. This matter is under further investigation. It also appears that further extensions of the theories and sources of information must be made before more exact determinations of dissociation constants in nonaqueous solutions can be made upon the basis of the Debye-Hückel equation.

[12] Goldschmidt, Z. physik. Chem., 94:46 (1916).

[13] Larsson, Thesis, Kopenhagen (1924): "Untersuchungen uber die electrolytische Dissoziation einiger Electrolyte in aethyl alkoholische Losung." See also Kolthoff, J. Phys. Chem., 35:2732 (1931).

[14] Walden, "Elektrochemie nichtwassriger Losungen," 1924, p. 361.

CONCLUSIONS AND SUMMARY

The dissociation constants of trichloroacetic and monochloroacetic acids have been evaluated by means of the extrapolating function, $\log k - \frac{2 A \sqrt{2\mu}}{1 + \alpha \sqrt{2\mu}}$, from measurements of the electromotive forces of cells without liquid junctions. The method is based upon thermodynamic principles and upon assumptions which appear justified by experimental evidence. The dissociation constant of trichloroacetic acid has been found to be 3.236×10^{-6} and that of monochloroacetic acid 5.224×10^{-7} when lightly coated platinum black electrodes were used and $5.720 + 10^{-7}$ when platinum electrodes coated with bright platinum were employed.

Submitted to the Department of Chemistry of Indiana University by Frank J. Welcher in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

PAPERS FROM THE PROGRAM OF THE GEOLOGY AND GEOGRAPHY SECTION

THE GARRETT MASTODON

PAUL F. SIMPSON, Indianapolis

To the writer fell the responsibility of directing the excavation of a comparatively well preserved Mastodon specimen, for which the name *Garrett Mastodon* is proposed. This skeleton was discovered by Mr.

Fig. 1. Part of the bones of the Garrett Mastodon before they had been moved from their original position.

Paul Dunn, a highway worker, on September 29, 1933, while he was probing in the ground for a drain tile. When the rod struck a solid object, he dug for the expected tile, and found instead a tooth. Further digging uncovered three other teeth, fragments of the lower jaw, and part of the pelvic girdle, which were removed, and several other bones which were covered again and left in place.

The find was located in the southwest quarter of the southwest quarter of section 10, Keyser township, Dekalb County, two miles south of Garrett, on the right-of-way of U. S. Road 27.

Mr. Verne Patty, of the State Museum, and the writer reached the scene October 5, and with the assistance of Mr. Dunn, Mr. L. L. Searfoss, highway patrolman, Mr. Fred Ballentine, Mr. Marion Hoyles, and Mr. Charles DeVeny, uncovered the remaining bones. Because of the

interest aroused among local persons, it was deemed advisable to complete the excavation at once, in order to prevent others from taking the smaller parts. The excavation was completed on Friday afternoon, October 6, and the bones were brought to Indianapolis October 7.

It was impossible to learn from the arrangement of the skeleton what position the animal had been in when it died, and it is likely that the bones were disarranged by other animals before they were buried beneath the marly clay in which they were found. The tusks and head were in poor condition, and the shoulder blades and pelvic bones were somewhat broken; practically all of the other bones were sound. The tusks could not be measured accurately, but were approximately seven feet long. Only five teeth were recovered, and these show evidence of great wear. The vertebrae were in two sections about eight feet apart, and the head was upside down, as though it had been thrown back over the left shoulder. The bones averaged four feet in depth beneath the surface, at about the present ground water level. The surface material was muck, and apparently the spot had been within the edge of a swamp.

Associated with the bones was a piece of wood about three feet long and two and one-half inches in diameter. This has been identified by Dr. Samuel J. Record of the School of Forestry of Yale University as a branch of *Larix americana*, or tamarack. Some of the mud which coated the bones has been examined by Mr. P. K. Houdek of the botany department of the University of Chicago, who reported that pine, fir, and oak pollen were present in it.

A mixture of methyl acetone and celluloid has been found satisfactory as a preservative, and the bones are being coated with this after they have thoroughly dried. No arrangements have been made for the mounting or permanent storage of the skeleton, but it will be stored temporarily in the State Museum.

SOME UNUSUAL GEODE FORMS

William P. Von Osinski, Indiana University

Some time ago, Dr. C. A. Malott brought a peculiar form of geode to the writer's attention. Through his co-operation, the locality of occurrence of the geodes was found and a large number of specimens were collected.

The geode, as usually described, is a sub-spherical body consisting of a shell of compacted crystalline quartz, inside of which occurs crystals of quartz, calcite, and occasionally, other minerals. There may or may not be a cavity. The new form little resembles the normal, rounded geode. The unusual geodes are either sliver-like or elongated, faceted wedges which fit tightly together and make up the whole of a lens in the parent formation (See B, Fig. 1). They do exhibit, however, true

geode structure. The cavity is present in most of the larger specimens and even in some of the smaller slivers.

The wedges range from one and one-half inches to five inches in length and from three-quarters of an inch to three inches square at the butts, from which they taper to more or less of a point. The large ends of the wedges are oriented alternately toward the top and the bottom of the lens in which they occur (See C, Fig. 1). The slivers are usually thin enough to be slightly translucent. They range from three-quarters of an inch to three inches in length. The individual pieces fit very closely together, but a few blows with the hammer cause them to separate along the facets, each piece a true geode (See D and E, Fig. 1).

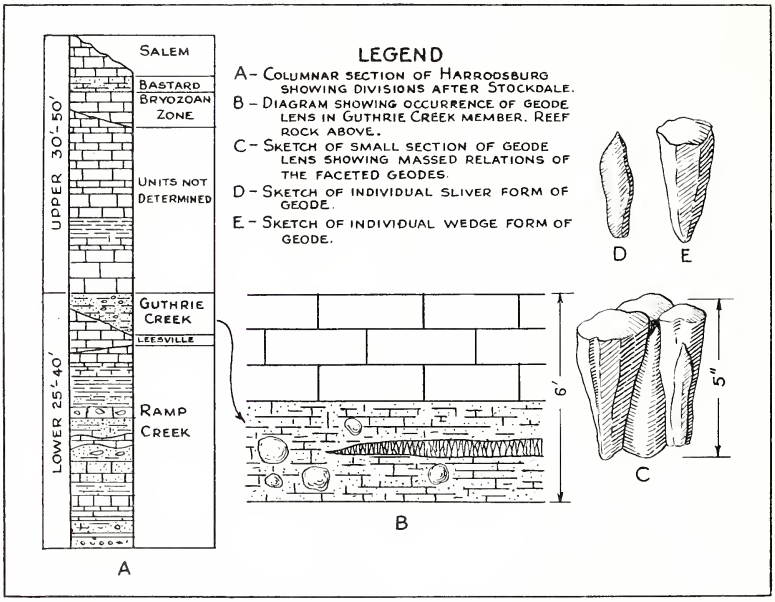


Fig. 1. Illustrating the faceted geodes and their occurrence in the Harrodsburg limestone.

The locality where these peculiar geodes were found is in the west bluff of Stouts Creek Canyon, a short distance downstream from the ford crossing just west of the Park School, in section 19, T. 9 N., R. 1 W., about two and one-half miles north of Bloomington, Indiana. They occur a little below the middle of the Harrodsburg limestone, in a silty zone just below a massive, reef-like structure described by Beede.[1] The silty zone appears to be the Guthrie Creek member of the lower Harrodsburg as described by Stockdale[2] (See A, Fig. 1).

The elongated geodes seem to have had their origin in the same processes which accounted for the sub-spherical variety which occur at

[1] Beede, J. W., 39th Ann. Rept., Indiana Dept. Geol. Nat. Resources, p. 195, 1914.

[2] Stockdale, P. B., Stratigraphic Units of the Harrodsburg Limestone, Proc. Indiana Acad. Sci., 1929.

the same horizon, both up- and down-stream from the lens in the silty zone or the Guthrie Creek member of the Harrodsburg. Indeed, the elongated types show a tendency to round at the butts of the wedges. It seems evident that the elongated species are a result of close compaction upon one another; this compression has been sufficient to prevent the normal rounded or sub-spherical form. The individual geodes, when pressed upon one another, developed the elongated form with the facets and the thin sliver form because of lack of space, in a manner similar to the growth of the hexagonal corals, each geode having its individual casing of crystalline quartz. Each geode is therefore a complete specimen. The lens encompassing them is a closely packed mass of individual geodes.

PAPERS FROM THE PROGRAM OF THE PHYSICS SECTION

MULTIPLE RESONANCE IN VIOLINS

R. B. ABBOTT and R. O. JENKINS, Purdue University

The object of this investigation was to determine the lower resonance frequencies of the air cavities of violins when the tops and bottoms were not allowed to vibrate and also when they were allowed to do so. It was thought best to use a siren, a vibration meter and tuning forks for determining resonance frequencies rather than a telephone receiver and variable oscillator such as used by F. M. Chambers. The work was carried on because there was much uncertainty regarding the position of strong resonance bands and points for low frequencies, which aid in strengthening the fundamentals and lower partials of the violin tones. This object was accomplished by the locating of one strong band, two fairly strong points and one weaker point all below 1,100 vib. per sec. Methods and results are given in the following report.

To keep the top and bottom of a violin from acting as diaphragms coupled to the air cavity, it was buried in sand leaving only the F holes uncovered. Tuning forks of different frequencies or a siren of variable frequency were held over the F holes and resonance frequencies noted for maximum reinforcement of the resulting sound. As a result, one strong band was located at 256 to 340 vib. per sec.; strong points were found at 512 and 728 vib. per sec.; one weaker one was evident at 1,024 vib. per sec.

With the violin out of the sand and free to vibrate, the above methods were repeated, also a vibration meter was used to indicate maximum vibrations of the top and bottom of the violin when a variable frequency sound was produced in the neighborhood by a siren or organ pipe. A number of violins were tested in this way with the result that approximately the same resonance band and points were located. However, the resonance was stronger.

The object of this investigation included an attempt to check the experimental results with the present acoustical theory. The values of the conductivity of F holes and the volume of the air cavities of violins were determined experimentally for use in the following theoretical work. Calculations were made from the theory of Helmholtz resonators, first, assuming that the cavity of the violin acted as a single resonator; second, that it acted as two parallel resonators.

In the first cast the results were as follows: The conductivity of the F holes was found to be $K = 4.68$ c.g.s. units and the volume of the cavity $V = 1{,}970$ cu. cm. The velocity of sound C at 20° C. was 34,500 cm. per sec. The theoretical resonance frequency is $F = \frac{C}{2\pi}\sqrt{\frac{K}{V}}$. This gives $F = 268$ vib. per sec. which falls within the lower limit of the resonance band.

In the second case, the air cavity was assumed to be divided into two parts by a plane through the middle of the F holes and considered as two parallel resonating cavities. The formula for calculating the resonance frequency in this case was developed from the analogy to similar electrical circuits with parallel connections. In this electrical case for resonance the current is all in phase with the electromotive force and the wattless component is zero. This condition for two parallel circuits with reactances X_1, X_2 and impedances Z_1, Z_2 is expressed as follows:

$$I_1 \sin \theta_1 + I_2 \sin \theta_2 = \frac{EX_1}{Z_1 Z_1} + \frac{EX_2}{Z_2 Z_2} = 0.$$

When the analogous acoustical terms are substituted in the above equation and the proper violin data are substituted for the constants its solution gives the resonance frequency $F = 334$ vib. per sec., a value which falls within the upper limit of the resonance band found by experiment. This suggests that this resonance band is due to multiple resonance between the limits of the above frequencies.

After investigating many violins of both old and modern makes, it was found that this strong resonance band occurs in all models approximately between the same frequency limits. This result must be so, for the reason that violin makers have always thought that they must keep the size of the F holes and volume of the inside of the violin the same, regardless of other modifications in models.

A NEW FOCUSING DEVICE FOR ELECTRON DIFFRACTION

William I. Caldwell, Purdue University

Up to the present time all the methods used to study crystal structure by electron diffraction have been adaptations of x-ray methods. Although these methods have been successful they all possess inherent difficulties. These difficulties arise from the low penetrating power of the electrons and from the short wave lengths of the electrons at moderate velocities. An attempt has been made to find a method that will obviate, in so far as possible, these difficulties.

The diffraction of radiation by powdered crystals is usually considered as the summation of a large number of Bragg reflections. However, the work of Brentano[1] suggested another viewpoint which, it can be shown, is applicable to all diffraction methods. Brentano's reasoning was somewhat as follows:

Let ABCD (Fig. 1) be a section of a toroid, the surface generated by rotating the arc of a circle ABC about its chord AC. EF is tangent

[1] Phy. Soc. London 38:184, 1926.

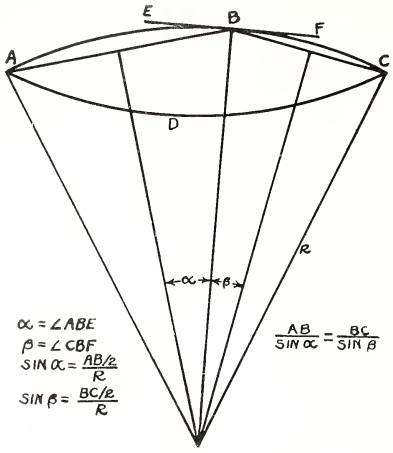


Fig. 1.

to the surface at B. $<ABE = \alpha, <FBC = \beta$. A line drawn from A to any point on the surface will make a constant angle with a line from C to the same point. Since this is constant, radiation from A incident upon crystals on the toroid will be focused at C if $n\lambda = 2d \sin \left(\frac{\alpha + \beta}{2}\right)$. Let R be the radius of the toroid. From the illustration it is seen that sin α = AB/2R and that sin β = CB/2R.

It follows that AB/sin α = BC/sin β.

Obviously this condition must be fulfilled by any method for sharp diffraction patterns to result.

Brentano's focusing condition suggested at once a possibility for a new electron diffraction method. In this method, figure 2, the surface of a toroid is used to hold the crystalline meterial with a point source of electrons at one end of its axis and a fluorescent screen or collector at the other. By changing the accelerating voltage of the electrons through

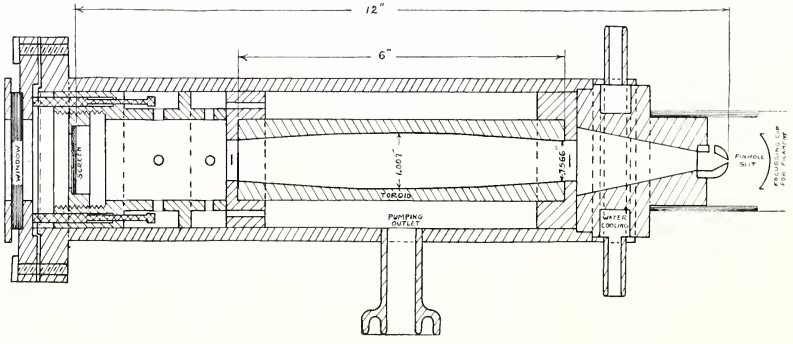


Fig. 2.

a suitable range the wave length of the beam will change and the different planes will in turn produce point patterns. By observing the accelerating voltages at which the point patterns are produced, the crystal structure can be determined. This method has the advantage that the intensities can be measured directly with an immobile collector, also that of great intensity since the electrons are focussed at a point instead of being distributed in a ring. The low penetrating power of the electrons will not cause difficulties as the electrons will be reflected instead of being transmitted.

A camera has been built on this principle, figure 2.

MAGNETIC EFFECT ON A VIBRATING QUARTZ CRYSTAL EXCITED PIEZO-ELECTRICALLY

SAMUEL H. CORTEZ, Indiana University

INTRODUCTION

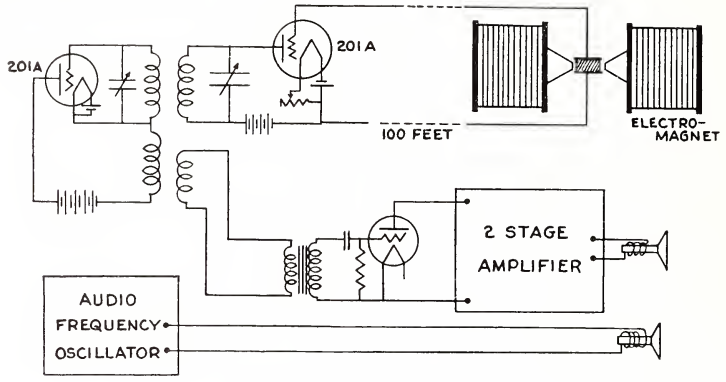
Work carried on during the last few years has been quite exhaustive in determining the various properties of quartz. Its wide use in oscillators of constant frequency has necessitated a knowledge of the various factors which control its natural frequency. Much work has been done and many articles have been written regarding temperature effects.[1] None, to the knowledge of the writer, has appeared regarding a magnetic effect. It was therefore thought advisable to investigate this possibility.

DESCRIPTION OF APPARATUS

The apparatus used in investigating the magnetic effect consisted of four vacuum tube circuits and an electromagnet. One of the vacuum tube circuits acted as a piezo-electric oscillator, the improved Pierce circuit being used. Two of the vacuum tube circuits were Hartley oscillators, one for radio frequencies, the other, using an iron core coil, for audio frequencies. The other radio circuit was a three stage amplifier and detector. The piezo-electric oscillator was coupled inductively to the Hartley radio frequency oscillator, which was in turn inductively coupled by means of a coil and an input transformer to the audio amplifier detector. A loud speaker was connected to the output terminals of the amplifier. By adjusting the frequency of the Hartley oscillator to within 1,000 cycles of the frequency of the piezo-electric oscillator, a beat frequency electric current was produced which, after passing through the amplifier, was converted by means of the loud speaker to acoustic energy in the form of a sound wave whose frequency was the same as that of the beat frequency current. A telephone receiver was connected in the plate circuit of the Hartley audio oscillator which

[1] Paul Vigoureux. Quartz Resonators and Oscillators, p. 19.

converted the energy of the audio frequency plate current into acoustic energy in the form of sound waves of the same frequency as the plate current. By adjusting the frequency of the Hartley audio oscillator to within a few cycles of the note from the loud speaker an audible beat note between the two tones was detected by the ear. This beat note, by suitable adjustment, was made to have a frequency of from 10 to 30 cycles per minute, which enabled one to count them easily. Any change in the frequency of either of the three oscillators was readily detected by a corresponding change in the frequency of the beat note of the sound waves. A complete circuit diagram of the set-up is shown in the following figure.



PROCEDURE AND RESULTS

The crystal used was a bar of quartz whose length in the *t* direction was 9 cm., breadth in the *o* direction 2.6 cm., and thickness in the *e* direction 1 cm. The natural frequency was 30 K.C. The crystal was mounted with its brass electrodes between the poles of the electro-magnet so that the magnetic lines of force were in the t direction. Upon closing the switch controlling the current to the electro-magnet an abrupt increase in the number of beats per second was observed. This increase could be obtained only when the magnetic lines of force were in the direction of the greatest motion. For when the crystal was orientated to permit the magnetic lines of force to be in the *e* and *o* directions no increase in the number of beats was observed upon closing the switch. The fact that the effect was obtained with the field only in one direction eliminated the possibility of the abrupt change being caused by an electromagnetic coupling, as no changes were made in the apparatus during the various trials except the orientation of the crystal in the various directions.

To eliminate all possibility of coupling and to determine whether the field strength increased or decreased the effect, the crystal leads were extended about a hundred feet to a larger electro-magnet in a room on the next floor. The experiment was repeated and the same results obtained. No appreciable difference due to the stronger field was observed. In the first case the field was about 1,500 gauss and in the second case about 4,500 gauss. Several sets of data were taken by counting the

beats for ten second periods with the magnet current flowing and with it off. The difference between these readings gave the increase due to the field. The average for all the sets was 5 cycles increase for the ten second periods, making an average increase of 0.5 cycles in 30,000. Crystals of 40, 70 and 100 K.C. natural frequency were tried, but each gave negative results.

Discussion of Results

When a quartz bar is caused to expand and contract as in a piezo-electric oscillator, electric charges of first one sign and then the other are liberated on the faces at the extremities of the electric axis. Since the charges change sign at a rate equal to the natural frequency of the crystal there must be a transfer of electricity of some kind or other. This transfer is supposedly made by a change in the internal structure of the crystal. This would involve a motion of the atoms, which being charged would constitute a minute electric current. The conductor of such a current when placed in a magnetic field would experience the usual thrust perpendicular both to the direction of the current and to the magnetic lines of force. Also according to modern theories of atomic structure the atom consists of electrons which rotate around a positive nucleus. These rotating electrons really constitute a current. The magnetic field would affect the direction of this current and thereby distort the normal orbits of the electrons. The net result of these two effects might be to change the modulus of elasticity and hence the natural frequency of the crystal.

Acknowledgments

The writer wishes to acknowledge his indebtedness to Dr. A. L. Foley, who suggested the problem, and who followed its progress with kindly interest and helpful counsel. He is also grateful to the other members of the Department of Physics at Indiana University who aided in various ways.

EFFECT OF SOUND ON SPACE CURRENTS

Seth Earl Elliott, Butler University

The object of the following investigation was to find a desirable method of measuring sound intensity. It was thought if sound could, somehow or other, be used to modify space currents in air, it might be possible to eliminate some of the objections to previous methods of measuring sound intensity. Three different methods were tried: (1) The effect of sound on the path of the electron current given off from a hot Nernst filament; (2) the effect of sound in modifying the amount of space current given off from a fine hot platinum wire; (3) the effect of sound on electron radiation.

The Effect of Sound on the Path of the Current from the Nernst Filament Circuit and Theory. The positive and negative discharge of a Nernst filament was studied by Gweln Owen.[1] The diagram of the circuit which we used is given in figure 1. D is the heated Nernst filament which is mounted vertically, B and C are two safety razor blades insulated from each other by a mica film at a distance of 1 mm. and mounted on the table of a traveling microscope with their edges vertical.

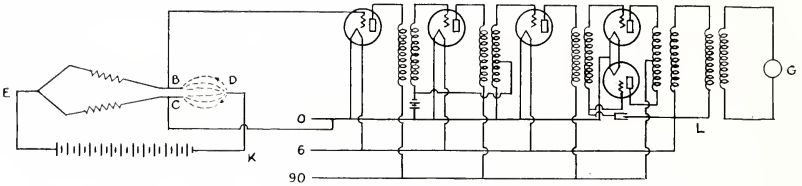


Fig. 1. EK is Nernst Filament Circuit. LM is step down transformer. G is hot wire instrument.

The theory of the circuit is as follows: B and C are the sharp edges of the razor blades. By imposing a difference of potential of 1,500 volts between D and edges of the razor blades a field of the nature of that shown in the diagram would exist between B, C, and D. It was thought that the discharge from the Nernst filament would follow these lines rather closely. The photographs taken by Dr. Foley in an unpublished investigation on electric discharges suggests that the stream of ions in air maintained quite definite lines of flow. It was therefore thought that by passing sound waves perpendicular to the Nernst filament and razor blade edges, it might be possible to find a proper potential and position of blades and filament such that the sound wave (by actual mechanical displacement or by changing the dielectric constant due to compression and rarefaction) might cause an increase in the number of ions in one path and a decrease in the other path; say, an increase in DC and a decrease in BD. There also might be slight change in surface temperature which would change the radiation of the Nernst filament. Dr. Foley has shown by his condenser microphone that such an effect as changing the dielectric constant exists. Assuming that there was sufficient directive action on the ions by the electric field to keep the two streams in well defined paths, there would be a current of different strengths in R_1 and R_2 and hence a difference in potential between B and C. When the mechanical state of affairs is reversed by the sound wave then there would be a reversed difference of potential from B to C. Suppose current in R_1 is i_1, and in R_2 is i_2, then the difference in potential between B and C would be equal to $R_1\ i_1 - R_2\ i_2$. This difference in potential would change with the same frequency as the sound waves causing it and would depend in magnitude on the amplitude of the sound vibration. This was tried under a variety of circumstances and no effect was observed on the milliameter.

[1] Phil. Mag. 8, 236, 1904.

Conclusion. Failure to observe any effect is probably due to the collisions between ions and molecules, keeping the boundaries of the two different paths of such an irregular nature that a small shift would have too small an effect on the strength of the current in either path to cause a detectable difference in potential between B and C. There would also be a question of phase relations among the three possible effects mentioned at the beginning; namely, change in the path due to mechanical displacement, change in path due to change in dielectric, and change in temperature. The change in temperature would undoubtedly be extremely small in a filament as large as the Nernst filament used and could at best be a surface effect only.

Effect of Sound on Ionization Current from Incandescent Platinum. It is a well known fact that heated solids give both positive and negative ionization currents. Elster and Geitel[2] investigated this phenomenon very thoroughly. Rutherford[3] measured the discharge, both positive and negative, from platinum under various conditions; namely, variation of current with potential, variation of current with distance between discharging and receiving plates, variation of current with temperature of discharging plate.

There are a number of factors which influence the discharge; namely, pressure, long continued heating, absorbed gases, dust, and gas in which the plates are placed. The phenomenon is apparently very complicated. J. J. Thompson says, "The initial rapid decrease with time is presumably due to the removal of the potassium or sodium, which forms the ions from the surface layer of the metal."

D in cm.	Current	iD
2	18,800	150,000
3	2,690	72,600
4	835	53,400
5	296	37,000
6	156	33,700

The current falls more rapidly than the equation indicates. No allowance was made for temperature between the plates. When the equation was derived, this would account for the difference in data and experiment.

H. A. Wilson[4] has shown the relation between positive and negative currents. He used two concentric platinum cylinders of diameters .75 cm. and .3 cm., respectively, in air at atmospheric pressure. The outer tube was the hot electrode as in the diagram shown below, Fig. 2.

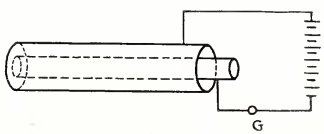


Fig. 2.

[2] Wied. Ann. 16, 193, 1882; 19, 588, 1883; 22, 123, 1884.
[3] Phys. Rev. Vol. 8, 1901, p. 321.
[4] J. J. Thompson cond. of Elect. Through Gases 397.

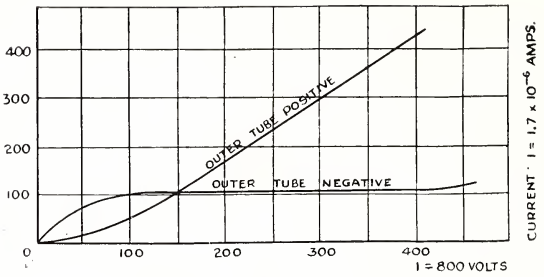


Fig. 3.

We are especially interested in Fig. 3 which calls attention to the curves of H. A. Wilson. We should especially notice that the positive current at these temperatures is much larger than the negative. We had these factors in mind when we designed the apparatus for the present experiment.

KL, Fig. 4, is a battery for heating a fine platinum wire (.0003′ in diameter) and 3 cm. long. MN represents a tin plate .2 cm. from the wire. The remaining part of the diagram is the conventional method of representation and is self-explanatory.

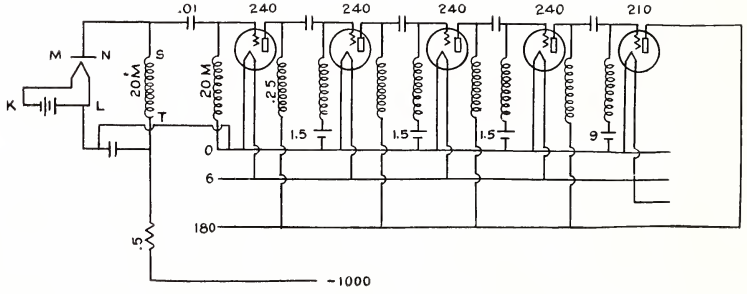


Fig. 4.

Sound waves passing the heated platinum wire should cause variations in the temperature of the wire, which, according to the theory, should cause variations of the space current from the platinum filament to the plate which was maintained by B batteries at a negative potential of 1,000 volts. This current passing through ST would impose a varying potential between the grid and the filament of the first two-hundred-forty tube in the amplifying circuit. In short, this is practically a two electrode tube operating at atmospheric pressure instead of in a vacuum. The output of the amplifier was connected to a sensitive head-set with sufficiently long heads so that one could make observations across the hall. Organ pipes of various pitch were sounded but no effect could be detected. The sensitivity was ascertained by several different methods.

We think that we have arranged the apparatus in all details to give the maximum effect consistent with practical construction; namely, a wire .0003′ in diameter to increase the amount of heating and cooling, a foot of wire to supply a relatively large surface, 1,000 volts from plate to filament to cause a large current to flow, .2 cm. distance between wire and plates which increased strength of field at surface of the wire (one would expect a steep curve and hence a large change in current with small change in temperature), small tin plates and quartz insulation to keep the capacity as small as possible, negative potential on the plates as the positive ion current is much larger at lower temperatures, a high voltage amplifier, and sensitive head set.

We therefore conclude that whatever effect may exist as a result of sound passing a hot platinum wire used in this manner is, being considerably smaller than the effect, due to the unavoidable capacity of the circuit, therefore too small to be of any practical value.

Effect of Sound on Electron Radiation from Active Wires.

Theory. Richardson[5] has derived a formula for electron radiation which checks very well with experimental measurements; $i = aT^{\frac{1}{2}} \varepsilon^{\frac{-b}{T^6}}$ in which i is electron current; a is a constant; T, absolute temperature; t, base of the Naperian logarithms and b is another constant. Accurate experiment, however, shows that the formula is more nearly correct with T^2 instead of $T^{\frac{1}{2}}$. The factor $\varepsilon^{\frac{-b}{T}}$ increases so rapidly with the temperature that either $T^{\frac{1}{2}}$ or T^2 has very little effect on the value of i.

Since the value of i varies rapidly with the temperature the idea occurred to Dr. Foley that we might heat a fine wire and then modify the electron current by sending sound waves past it. If this modification was sufficiently great, we might be able to detect it by means of an amplifier. A business concern had presented a fine wire of secret composition to Dr. Foley. Their representative recommended it as having the properties which we desired, namely, a small diameter (.0008′) would give a profuse electron current, and would stand red heat in air at atmospheric pressure for about six hours.

Twelve of these wires about one inch long were mounted in a plane parallel to each other. A similar set of platinum wires were mounted in the same manner. The two sets of wires were mounted with their planes parallel and with means for adjusting the distance between the planes, Fig. 5.

Let A B represent the active wires; C D the platinum wires. E and F were connected to grid and filament of the first tube in Fig. 4. The active wires were raised to red heat by the battery K L, a positive potential of 1,000 volts was placed on the platinum wires. Sound from an organ pipe was then passed by the wires. No effect could be de-

[5] Wilson Modern Physics, p. 49.

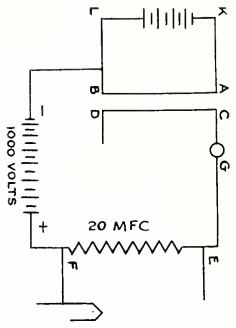


Fig. 5.

tected in the output of the amplifying circuit nor was there any change in the space current indicated by G.

SUMMARY

We have thus tried three different methods for using space currents in air at atmospheric pressure to detect sound waves.

The first method was an attempt to direct the discharge from a Nernst filament into two close, nearly parallel paths. It was thought that by mechanical impact due to sound waves passing through these paths some of the ions would be driven from one path into the other and vice versa, and that these variations in the current caused variations in the potential across a high resistance through which the current was flowing. Any variable electromotive force thus generated was imposed on the input of an amplifying circuit. The output was connected to a telephone receiver.

The second method was an attempt to vary the ionization current from incandescent platinum wires by changing the temperature of the wires by the fanning effect of the sound waves.

The third method was an attempt to modify the electron radiation from an activated wire by changing the temperature due to the passage of sound waves. The same method for detecting the effect was used in the last two cases as in the first.

No sound was heard in any of the three cases. The telephone receiver had a current sensitivity of .0000027 amp. or .00352 volt. The amplifier used in the case of the active wire and also for the Nernst filament had a voltage amplification of about 6,000. Let E stand for the minimum voltage which if impressed on the input of the amplifier can be heard in the telephone. Then $6{,}000\ E = .00352$ or $E = .00000058$. In the case of the Nernst filament if we let i equal the varying part of the current, the voltage impressed on the amplifier would equal 30,000,000i. $30{,}000{,}000i \times 6{,}000$ would then equal the voltage impressed on the telephone receivers. Then the equation $30{,}000{,}000i \times 6{,}000 = .00352$ or $i = 2 + 10^{-14}$ amps defines the maximum current which could flow through the 30,000,000 ohms and still not be heard in the telephone receivers.

That is, any variation caused by the sound on the discharge from the Nernst filament must have been less than $\frac{2}{3}$ of 2×10^{-14} or $\frac{4}{3}$ of 10^{-14} amps, since the current was passing through $\frac{2}{3}$ as much resistance.

The resistance coupled amplifier used in the case of the ionization current from incandescent platinum was considerably more sensitive than the other two cases mentioned. It was so sensitive that unavoidable capacity changes due to the circuit itself caused an audible tone in the telephone receivers.

We conclude that whatever effect there may be in any of the three cases, it is too small to be of any practical importance when used with materials and apparatus now available.

The writer of this paper wishes to thank Dr. Foley, who directed the research, for his interest and helpful suggestions during the progress of this work, and also the other members of the staff, who from time to time have shown interest in the problem and have given many valuable suggestions. I wish also to thank the Messrs. Price, Buell, and Foreman for help in making observations with the telephone.

METHODS OF MEASURING SURFACE POTENTIALS

JOHN E. FERGUSON, Purdue University

In the study of frictional electricity we observe the existence of large potential differences only when two surfaces have been separated to a relatively large extent. If we can observe the existence of a small potential difference with the surfaces at a small distance apart, we can understand the large potential due to their separation. Based upon this principle, a method of measuring surface potentials was devised by Volta and later used by Pellat.[1] This method, known as the condenser method, consists of two parallel surfaces, one of which is fixed, and the other is caused to move so as to vary the distance between them. In this way, an existing small potential difference between the surfaces is magnified and the effect can be measured with an electrometer. By inserting a counter source of potential in the circuit, the two surfaces may be adjusted to the same potential whereby no effect is produced by their relative motion. The condenser method, though simple in theory, has proved very delicate in operation. If one of the surfaces is a solution and the other a metal plate, it was found that the adsorption of moisture on the surface of the metal affects its potential to a considerable extent.

A second method has been used where a solution is concerned[2] and consists in measuring the potential difference between two flowing solutions. One of the solutions flows down the inside wall of a glass tube,

[1] H. Pellat: Ann. de Ch. et Phys., 24:5, 1881.

[2] Kenrick: Z. Physik Chem., 19:625, 1896.

the other, in the form of a jet, through the air space in the center of the glass tube. The results obtained by this method have not been consistent, and it is also difficult to separate the so-called ballo-electric effect, due to the breaking up of the jet, and the potential which is to be measured.

A third, and perhaps most convenient to use, is known as the ionization method.[3] It is similar to the condenser method with the exception that the surfaces are fixed and the space between them is made conducting by the use of some source which will ionize the air space. Radioactive materials are well suited for this purpose. However, such radioactive substances which ionize a small space have been found to give more consistent results. Polonium and uranium can be used, since they emit only the alpha particles which are completely absorbed in less than two inches of air.

We have used the ionization method for measuring the surface potentials of solutions. Instead of using an upper plate, our upper electrode was a silver wire with a small silver bead on the end and upon which polonium has been deposited. A sensitive Lindemann electrometer was used and its deflection was brought to zero by means of a potentiometer. In all the measurements the electrode making contact with the solution was either a reversible electrode or a siphon bringing the solution in contact with a normal calomel cell. If the concentration of the experimental solution is varied, any change in the potential at the surface layer of the solution can be calculated, since the behavior of the reversible electrode is accurately known. In this way the change of surface potential can be studied as a function of the concentration of the underlying solution. For these results to be accurate we can easily see that the potential of the radio-active electrode must be constant throughout the measurement.

This arrangement was found to be subject to the same errors which have been mentioned before with regard to the condenser method, namely, that due to the adsorption of moisture on the surface of the upper electrode, its potential changes.[4] Other sources of error have been suggested by Williams and Vigfusson.[5] We observed in the course of our experiments that when the surface of the experimental solution was covered with a single layer of stearic acid molecules the potential difference in the whole circuit was nearly constant over a several hours interval. The effect of adding a larger number of layers did not change the final value. In order to eliminate the moisture effect on the upper electrode, the possibility of making use of the above observation was suggested by Dr. Lark-Horovitz.

In Fig. 1 is given the new arrangement which we finally used. The solution at the tip of the glass siphon was covered with several layers of stearic acid. The polonium covered bead ionized the space between the stearic acid layers and the experimental solution and was not metallically connected with either.

[3] Guyot: Ann. de Phys., **2**:506, 1924. Frumkin: Z. Physik Chem., **116**:485, 1925.
[4] Guyot: Loc. cit.
[5] Williams and Vigfusson: J. Phys. Chem., **35**:345, 1931.

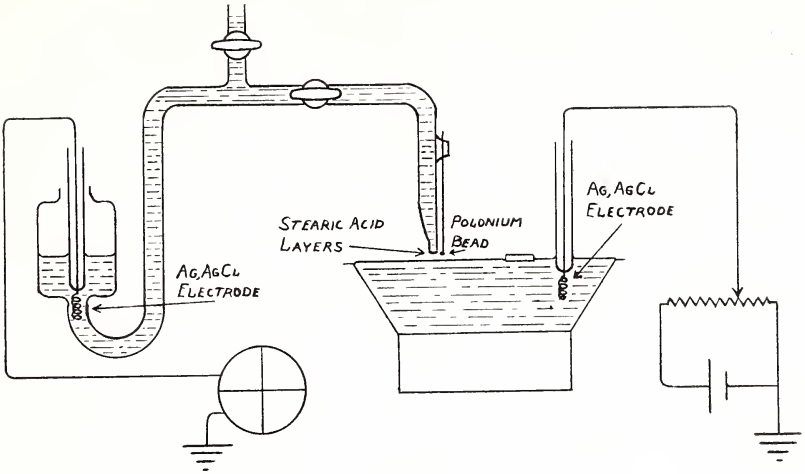


Fig. 1.

So far we have studied the relation between the concentration of the solution and the corresponding change in the potential of the circuit and found our results with the new arrangement much more reproducable, and constant with time, than with a metallic upper surface.

RADIO FIELD INTENSITY MEASUREMENTS ABOUT ATHENS, OHIO

D. B. GREEN and R. V. KELCH, Ohio University

A meter for measuring radio field intensities was constructed along lines similar to the instruments of Englund[1], Friis and Bruce[2], and Byrne[3].

The meter is essentially a vacuum tube voltmeter, reading the radio frequency voltage produced across the tuning condenser of the loop antenna circuit. It consists of a tuned loop antenna, feeding a superheterodyne receiver with an adjustable, calibrated attenuator in the intermediate frequency amplifier circuit. A calibrating oscillator furnishing a known voltage for comparison is coupled to the loop. Plate meters in the first and second detector circuits are used as volume level indicators.

[1] Proc. I. R. E. V. 5 P. 248, 1917.
[2] Bell Tel. Lab. reprint B-209, Sept., 1926.
[3] Ohio State U. Studies, V. 1, No. 4, Part 2, July, 1932.

Referring to fig. 1, the radio frequency signal, to be measured, of strength E volts per meter, induces a voltage, h E in the tuned loop circuit, where h is the effective height of the loop antenna. By the step-up action of resonance this voltage appears as Q h E across the tuning condenser C, where Q is the step up action of loop resonance. This voltage operates the first detector tube, whose output is controlled by the attenuator and amplified by the intermediate amplifier and fed into the second detector tube. The calibrating and beating oscillators are shown in the diagram. The loop can be shorted by the two switches, K_1 and K_2, without shorting the tuning condenser.

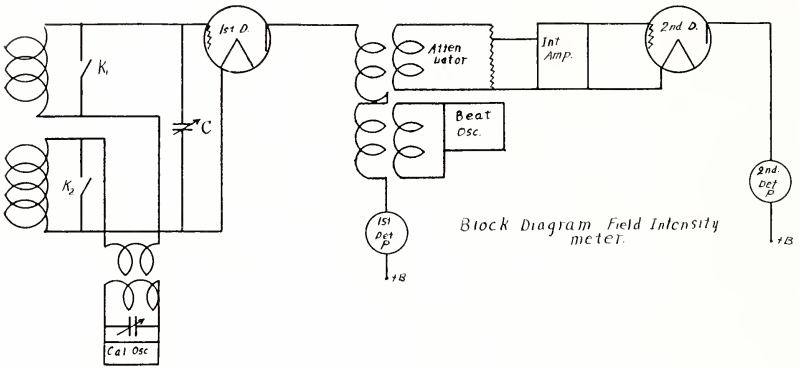


Fig. 1.

The first detector is calibrated as a vacuum tube voltmeter by impressing one volt A.C. upon the grid and noting the increase of plate current by meter No. 1. The method of measuring is, broadly, as follows: The amplified signal from the radio field is attenuated by an amount A_1 to produce a standard reading, say 100 microamperes, in the second detector plate meter. The standard voltage of one volt from the calibrating oscillator, tuned to the frequency of the radio signal is then applied to the loop and the attenuator adjusted by an attenuation of A_2 to give the same reading on the second detector plate meter. The loop is then shorted out by the switches, K_1 and K_2 and the standard calibrating voltage applied directly to the first detector without the step-up of loop resonance. The attenuator is again adjusted by an attenuation of A_3 to give standard reading on the second detector plate meter. The Q of the loop is found from the ratio of A_2 and A_3. The field strength in volts per meter can then be calculated from the three attenuator readings A_1, A_2, and A_3 and the calculated effective height of the loop antenna. The theory follows:

Since the same voltage is impressed on the second detector in all three cases, as indicated by the same reading of the plate meter, the input voltages on the first detector are proportional to the attenuator readings, required to reduce them to equality, so the voltage Q h E across the tuning condenser, caused by the distant station—

$$\frac{QhE}{1 \text{ volt}} = \frac{A_1}{A_2} \qquad \text{but } Q = A_2/A_3$$

$$\text{and} \quad hE = \frac{A_1 A_3}{A^2_2}$$

The field strength in volts per meter is obtained by dividing the volts induced in the loop by the effective height of the loop. This effective height is

$$h = \frac{2\pi NA}{\lambda}$$

where N is the number of turns in the loop and λ is the wave length of the signal and A is the area of the loop.

Some typical results are given in table I. Sixteen stations were studied, varying in field at Athens from 2400 to 2 microvolts per meter. Hill-top measurements averaged about 1.5 times as strong as the same signals measured in the Hocking River valley about 300 feet below the hilltops. Measurements of the same stations taken at Logan, Ohio, 22 miles northwest of Athens, but in comparatively level country, averaged 1.4 times as strong as the average between hill and valley measurements at Athens. This is after the Logan measurements had been reduced by the distance factor affecting some of the nearer stations. This is in accord with common report that all southern Ohio has poor reception. The difference is very noticeable when operating an auto radio en route from central to southern Ohio. The hilly terrain seems to attenuate the radio waves more than level country or else to screen all but the highest points from good reception.

FIELD INTENSITY MEASUREMENTS

Station	Distance miles	Field micro volts per meter Athens		Logan		Attenuation Constant Athens
		Hill	Valley	Distance	Field	
WKRC	120	110	77	115	120	.025
WAIU	65	220	120	44	310	.041
WLW	115	425	380	100	780	.030
WHAS	232	60	45	232	18	.030
KDKA	140	75	48	140	38	.038
WTAM	135	48	34	121	30	.039
WWVA	85	100	61	97	47	.05
WSAZ	65	70	25	73	.....	.057
Average[1]		138	98		192	

[1]Av. Corrected for Distance..... 153

Table II shows the constancy of the field produced by the better stations. The early morning and night figures show the results of fading. The night signal changed intensity by a factor of 10 often during a time of only a few minutes.

The curves of fig. 2 show the variation of the attenuation constant with frequency. To be sure, these figures were taken on different stations and all were assumed to have a quarter wave, grounded antenna in order to calculate their attenuation constant from measurements made at a single location but they show a definite tendency toward higher attenuation with higher frequency. Somerfeld[1] has arrived at the above conclusion, theoretically, and Byrne has verified it experimentally by measurements on Ohio broadcasting stations.

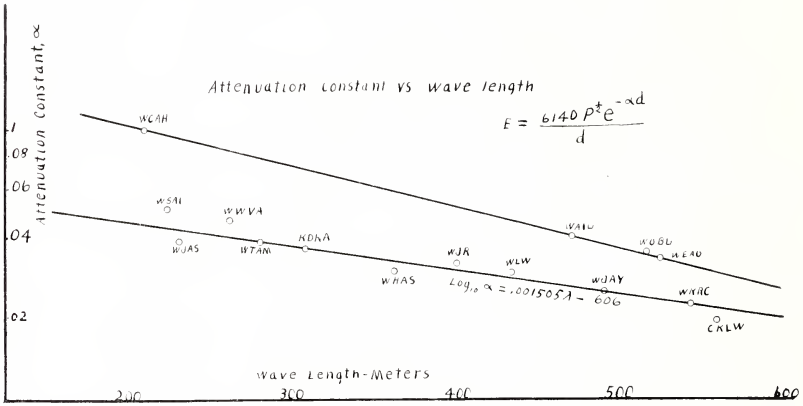


Fig. 2.

It is interesting to note that the attenuation constants for the stations whose signals followed the Hocking River valley, three Columbus stations from the northwest and a West Virginia Station from the south, were much higher than those stations whose signals came across the valley. These stations fell on a straight line which gave different constants in the equation deduced between frequency and attenuation constant, as obtained from semi-log paper.

It seems logical that ground losses might be classed as eddy current losses which always depend upon frequency.

TABLE II

VARIATION OF FIELD WITH TIME

WLW

Time 10 A. M.		May 1, 1933	
Day	Field	Hour	Field
May 4	485	6-20 A. M.	1700-550
May 7	485	9-00	680
May 9	435	11-00	680
May 16	485	12-00	680
		1-00 P. M.	680
		2-00	680
		4-00	610
		11-00	2400-240

[1] Ann. Physik. V. 4, No. 28, p. 665, 1909.

THE EFFECT OF POSITION UPON THE EFFICIENCY OF ACOUSTICAL TREATMENT[1]

Daniel L. Harmon, St. Mary-of-the-Woods, Indiana

In accoustical work it is assumed that the reverberation time is dependent upon two variables, namely, the total volume of the room and the total absorption of the surface exposed. This assumption leads to satisfactory results in the designing of new halls as well as in the correction of poor acoustics in old theaters, churches, lecture rooms, etc. The mathematical proof of the relation is direct and well known and the experimental derivation of the law was very ably contributed by W. C. Sabine in 1895. The rapid and rigorous development of the science of Architectural Acoustics since that time gives ample proof of the general accuracy of the Sabine Law. This law is expressed by the formula,

$$T = kV/A,$$

wherein, T is the reverberation time or the time required for the sound intensity to decrease sixty decibels, V is the total volume of the enclosed space, A is the total absorption present in the room, and k is a proportionality constant. This law requires a perfect diffusion of sound energy, a random distribution of the directions of the reflections, and no definite foci.

Now, even with the above enumerated conditions, are there not perhaps other factors which might affect the value of the reverberation time, T? Quite extensive researches have been made upon the effects of humidity, barometric pressure, temperature, pitch of sound, and other physical variations entering into the constant k. In fact these effects are quite definite and investigations are carried out with due regard for their constancy. Changes in volume, V, both in magnitude and in shape, have been exhaustively treated by many workers. Modern sound recording in the moving picture industry takes cognizance of the importance of size and shape in the designing of the studios to produce just the desired quality of music and depth of tone. The problem is reduced then to an investigation of the component parts of the factor A in the general equation. Until recently only one type of analysis has been made upon this factor and that is that the total absorption is equal to the arithmetical sum of the component parts, or,

$$A = a_1S_1 + a_2S_2 + a_3S_3 + \text{------}$$

wherein, a is the absorption coefficient of the sound-proofing material and S is the area of the surface covered. The absorption coefficients in sabines are taken from tables of physical constants and the areas are calculated for each type of treatment in the usual manner either from blue print specifications or from actual measurements. The numerical value of the constant k of the equation is equal to four times the natural

[1] Abstract of a thesis presented to the Graduate Council of Indiana University in partial fulfillment of the requirements for the Doctor of Philosophy degree.

logarithm of one millionth with this product divided by the velocity of sound in air.

The project discussed in this paper arose from the following general considerations: How does the coefficient of absorption depend upon the pressure of the incident sound energy? Will a given area of material separated into two parts produce the same correction as would the same area in a single unit? How does the efficiency of an absorber depend upon the direction and amplitude of the incident energy wave? Or, in short, is there an optimum position for the sound absorbing material? These problems are more or less involved and interdependent and hence have not been analyzed readily. James F. Mackell in 1931 completed a careful and conclusive determination of the effect of spacing upon the efficiency of absorbing material. C. A. Andree published in 1932 a mathematical projection of the problem of position of the material in correcting a cubical volume. This paper presents the results of tests made in variously designed rooms of different volumes upon the efficiency of a unit block of absorbing material when placed in different positions relative to the source, the reflecting walls, and the recorder. For each hall tested there will be found in Table A the average values of the reverberation time. A study of this table shows the apparently constant law of variation of efficiency with the position of the absorbing unit. In all tables and figures O designates the empty room, the letters a, b. - - - f show the successive positions of the absorbing unit, while the numbers 1, 2, and 3 designate the stations occupied by the investigator.

Preliminary Investigations. Before beginning the research various experiments were repeated in the reverberation room in Science Hall, Indiana University, hereafter referred to as Room No. 12. The source of sound was one of a series of rectangular wood organ pipes swinging from the ceiling and adjustable as to height and geometric location. These pipes were excited by means of a motor driven air compressor and the air pressure was controlled and measured in an anteroom adjoining the "live" room. When the organ pipe was excited by lung pressure the constancy of excitation was maintained by having a Thorpe Gauge properly connected to the mouthpiece of the pipe. A Jenkins and Adair condenser microphone was used as a sound detector. This was mounted upon a floor stand adjustable vertically and horizontally. The output of the one stage of amplification built into the microphone case was led to the anteroom where it was amplified and then measured with a vacuum thermocouple and microammeter. Observations were made using a battery operated amplifier as well as a Samson A. C. audio unit. A properly matched Brandeis headset could be substituted for the thermocouple-microammeter system when desired. Using this arrangement of apparatus and placing the microphone successively at the definite points marked in rectangular coordinates on the floor of Room No. 12 the factors governing the distribution of sound intensities in a room were studied. It was seen that definite standing wave patterns do exist under certain exact conditions. However, at some air pressures the quality and intensity of the sounds emitted by the organ

pipe were so unstable as to cause the pattern to change or creep quite rapidly. The time lag in the amplifier-microammeter system was greater than the time required for this change of intensity and hence entirely vitiated the readings. It was noticed also that the sound intensity near the walls changed continuously showing that the conditions in this border region are unstable and hence that the angle of incidence of the pressure wave with the wall is a varying quantity. This then, while eliminating the standing wave pattern method as a recording scheme in this research, proved, nevertheless, the importance of determining the dependence of absorption efficiency upon the conditions of incidence. While taking data in Room No. 12 the masking effect of a second continuously emitting sound source was clearly demonstrated. When the power vacuum cleaner system was in operation the percentage decrease in the duration of sound after cut-off was very evident and quite constant. The other method of recording data was the ear-chronometer scheme where the observer is in the room and measures the time, by means of a manually operated stop watch, from the sound cut-off to the threshold of audibility. In any investigation the recorded value is the average of at least two hundred separate readings and each reading is the mean of ten successive reverberation periods. Many checks seem to prove the dependability of this ear-stop watch method of measurement. One such check was made in Room No. 12. The head set was substituted for the thermocouple-microammeter in the anteroom and a series of reverberation periods were taken with the observer in this anteroom. The mean value checked favorably with that determined when the observer was in the "live" room. Hence in the subsequent investigations the ear-stop watch method was used entirely. In presenting the results of the main researches no regard will be paid to their chronological order. In fact the entire mass of data for the first three halls had been recorded and studied over several times before the relation emphasized in this report was noticed. Then the investigation was carried to the Music Hall and from there to the Commerce Hall where an extensive and precise set of data was recorded, which when worked out two days later was in exact agreement as shown in Table A.

Union Hall. The auditorium in the Student Union Building at Indiana University (Union Hall) is a rectangular room with a high, beamed ceiling, a small balcony, and an entrance vestibule. This room is quite live, even when filled with leather upholstered chairs, as it was when these data were taken. The three positions of the observer were: (1) standing at the rear of the hall near the entrance, (2) standing at the front stage at the speaker's position, and (3) sitting on a chair placed upon the absorbing unit. Of course it is to be remembered that the absorption represented by the observer's body changed position in each case, which might account for some of the general variation. However, since each separate set of data shows approximately the same variation as does the set of average values this change is immaterial. Other positions were tried, but owing to the geometric cross-section of the hall direct echoes interferred with the determination of the period by affecting the k of the Sabine equation rather than the A.

The absorbing unit used in this hall was composed of thirty square feet of asbestos wool in metal sections and fifty pieces of Quietile in one-foot squares. The large volume of the room reduced the percentage effect of the additional absorption introduced. Hence the unit had to be relatively large.

Room No. 12. In the "live" room in Science Hall, Room No. 12, besides the preliminary researches discussed in the introduction, two sets of data were recorded following the general scheme used in Union

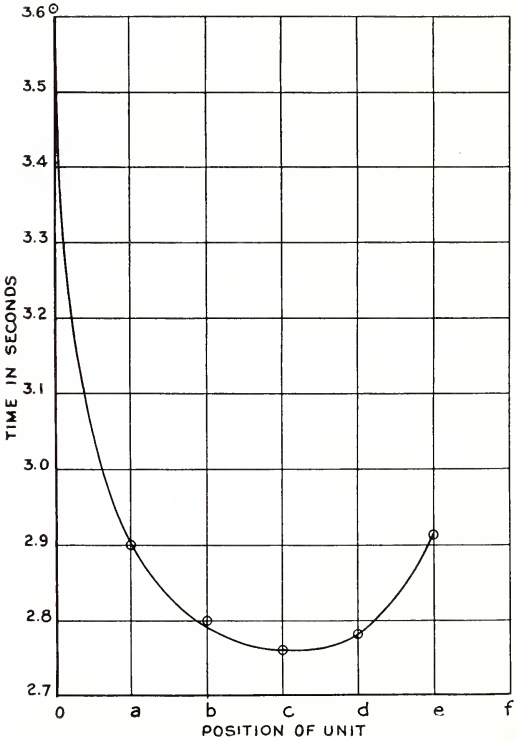


Fig. 1. Average reverberation time, room No. 12, empty.

Hall. The first observations were made using the room with no additional absorption present except the unit, which was placed upon the concrete floor. This arrangement gave the data tabulated in the second column of Table I and graphically presented in figure 1. Then the room was treated with hair felt, distributed as uniformly as possible, in order to bring the free period down to a value comparable, relative to the room size, with the free period of Union Hall. The data obtained then gave a curve with the same characteristics as that of figure 1. In this room the observer stood at a point near the east wall corresponding to the speaker's position if the room were to be used as a lecture hall.

TABLE I

Composite table of mean values of reverberation time.

Position of unit	Union Hall	Room No. 12	LeFer No. 500	Music Hall	Commerce Hall
o	3.87 s.	2.28 s.	3.11 s.	4.71 s.	4.31 s.
a	3.66 s.	1.63 s.	2.50 s.	4.38 s.	3.89 s.
b	3.59 s.	1.40 s.	2.32 s.	4.58 s.	3.76 s.
c	3.63 s.	1.43 s.	2.24 s.	4.38 s.	3.54 s.
d	3.63 s.	1.48 s.	2.18 s.	4.44 s.	3.57 s.
e	3.74 s.	1.49 s.	2.28 s.	4.62 s.	3.73 s.
f	3.83 s.	1.75 s.	2.44 s.	.....	3.82 s.

LeFer No. 500. The reverberation room of the physics department of St. Mary-of-the-Woods College (LeFer No. 500) is rectangular with the west wall, just a trifle higher than the east. It was possible in this room to make a check of each set of readings by taking advantage of the symmetrical design of the floor. With the absorbing unit, fifty square feet of Quietile, in a given position readings were taken with the observer first at position (1) and then at position (2). Then the final value of reverberation time taken at 1- -a should be the same as that taken at 2- -f, 1- -b as 2- -e, etc. (see figure 2). These expected checks were realized exactly.

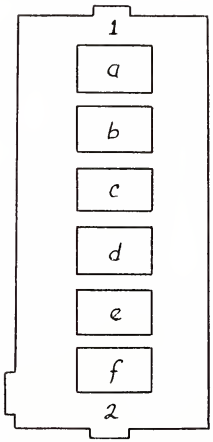


Fig. 2. Floor plan, LeFer No. 500.

Music Hall. Next a series of measurements was made in the Cecilian Auditorium, St. Mary-of-the-Woods College (Music Hall). This room is of a rather striking and very beautiful design. The floor plan is practically square. The pillars, built-in boxes, sloping floor, large curved balcony, and particularly the dome-shaped, stained glass ceiling make an effective combination for producing the acoustical qualities desirable for instrumental music. The room is fairly "live" for speaking, but this fault is partly overcome by the good sound distribution. The data

recorded in the fourth column of Table I were taken with the doors closed and the stage cut off by the heavy asbestos curtain. The absorbing unit was a large pile of various types of material moved from post to post with no change of arrangement within the unit. There is one point to be noted in particular and that is the unusual behavior at position b (see figure 3). After working up this data and noticing the eccentricity of this point b a second visit was made to the auditorium, and it was observed that there is an apparent loud area across the hall at b caused probably by the focussing of the reflected sound from the sloping balcony to this position. This is again an effect upon the constant k of the equation and the point b will have to be ignored in studying the effect of position upon the absorption A. The main point to be noted in this set of readings is that even with the odd ceiling and other features which might change the behavior of this room from that of the regular rectangular volumes studied before the variations of the average reverberation time with the position of the unit follows the same general law.

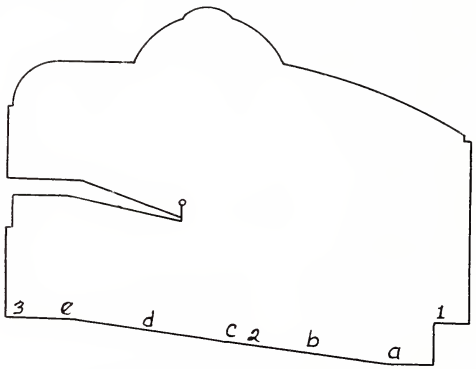


Fig. 3. Longitudinal section through center, Music Hall.

Commerce Hall. As a final check upon this position effect a very thorough test was carried out in the auditorium of the Commerce Building at Indiana University (Commerce Hall). In this investigation the absorbing unit was made up by arranging upon the seats and across the backs of the seats, in each position, a large amount of material of various types and coefficients. This arrangement took advantage of spacing effect, the exposure of all edges and both sides of each piece, and the effective "suspension in mid-air" of the unit instead of using it to cover a surface. It is evident then that if any change in the absorbing power is observed it must surely be due to the relative position of the unit, the reflecting walls, the source, and the observer. Column 5 in Table I shows the remarkable agreement of this data with that obtained in the other halls.

Summary. Even though the positions a, b, etc., are not absolutely identical in the several columns of Table I, a study of this table will facilitate the detection of the similarity of changes in the reverberation times recorded. A general statement of this agreement would be that

absorbing material is most efficient when placed in a position midway between opposite reflecting surfaces. The check is sufficiently complete with the unit placed upon the floor to imply that it would be the same if the symmetry were maintained and the unit placed upon the side walls or the ceiling. The observations made in Commerce Hall would seem to show that the most efficient position of the unit in the cases studied would be in the geometric center of the room.

In conclusion I wish to express my gratitude to Doctor Arthur L. Foley for his willing and helpful suggestions in the selection of this project and during the subsequent research. Thanks are due and gladly given Indiana University for the use of the facilities necessary to the experimental investigations. I wish to thank Doctor R. R. Ramsay for his suggestion in the arrangement of electrical apparatus and all other members of the physics department for innumerable hints and suggestions. And since it is impossible to measure the amount of assistance I have received from the many articles and books I have read I want to show my gratitude to some authors by the appended bibliography and to those unintentionally omitted by a sincere apology.

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AN X-RAY INVESTIGATION OF ORIENTATED DIELECTRICS

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Already in his papers on electromagnetic induction and its propagation Heaviside (1) indicated that a dielectric may exist in a state of permanent polarization similar to the orientation of the "elementary" magnets in a permanent magnet, and he called such a dielectric "electret." Investigations of these "electrets" have been carried out during the last ten years (2), but the nature of their properties is still doubtful. There are two different opinions to be found in the literature: According to the first theory, Eguchi, Meissner (2), the molecules or molecular aggregates are orientated by the electric field, and as a result application of mechanical stress distorting this orientation is supposed to produce a piezo-electric effect. According to the other point of view, Sato, Adams (2), the electrical effect produced by the field in a dielectric is of the nature of a displacement of ions: space charges may be set up and also phenomena which are more of the character of an electrolytic polarization may occur.

Experiments carried on in this laboratory have failed to reveal the existence of a genuine piezo-electric effect in the electrets and it was concluded that the field does not orientate the molecules and molecular aggregates. Since, however, X-ray evidence has been presented (3), which would indicate the existence of such an orientation due to the field, an X-ray examination of dielectrics solidified with field and without field has been undertaken.

The "electrets" were cast in an apparatus, the drawing of which is attached and is self-explanatory.

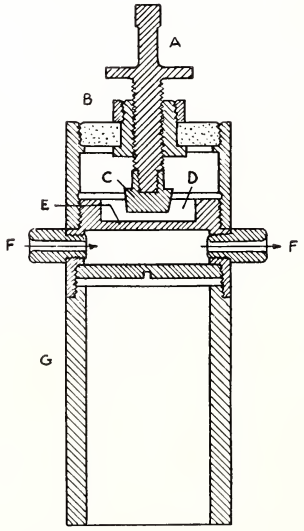

Fig. 1. The dielectric is filled into cavity D and heated by the heating coil kept in the container G. The electrodes C and E are then connected and solidification is started by having water circulated through F, assuring a definite temperature gradient. A, adjusting screw; B, insulator.

After the casting, the X-ray diffraction pattern of the samples was investigated with copper K-alpha radiation in an X-ray apparatus of our own design (4) and satisfactory exposures have been obtained in 20 to 40 milliampere hours.

We have investigated first pure paraffin in the form of thin transparent films (5).

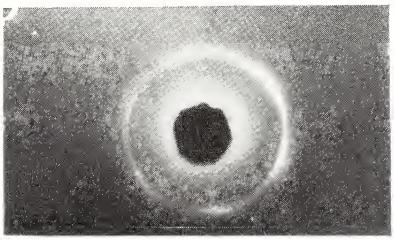

Fig. 2. X-ray diffraction of paraffin film on end of glass tube. Orientation pattern indicates formation of large crystallites and orientation of a long chain normal to the plane of the film.

We have also investigated thicker layers and some paraffin layers sliced with a microtome. Samples were cast in an electric field of 30 KV/cm or without field.

The following figures show that there is no indication of any change of orientation due to the electric field.

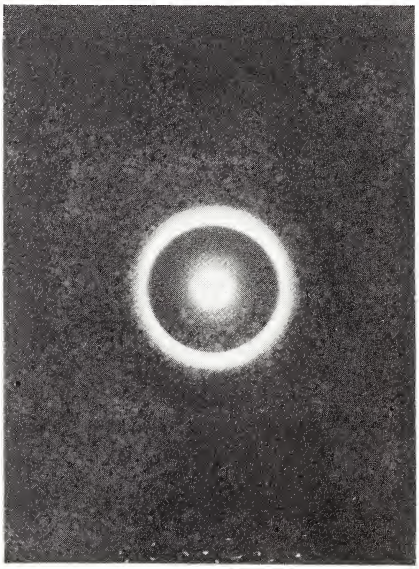

Fig. 3-A. Paraffin sample prepared in electret apparatus. No field. X-rays normal to temperature gradient.

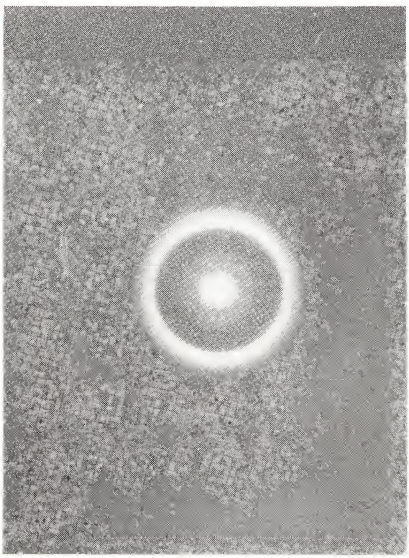

Fig. 3-B. Paraffin sample prepared in electret apparatus 30 KV/cm. field. X-rays normal to field and temperature gradient.

Note in both pictures the orientation pattern of second outer ring. Original reveals definitely also orientation pattern of inner ring.

In a similar way mixtures of caranauba wax with resin (45 per cent caranauba wax, 45 per cent resin, 10 per cent beeswax) have been prepared and again no evidence of any effect of the field was observed.

Since Meissner stated that a mixture of quartz powder with the dielectric exhibits even a greater piezo-electric effect than pure quartz crystals, such mixtures were also prepared. No definite evidence of any orientation of the quartz powder has been found.

Finally sulfur was cast with and without an electric field. In this case we found that large single crystals are formed during the process of solidification and that the mechanical effect as produced by the field

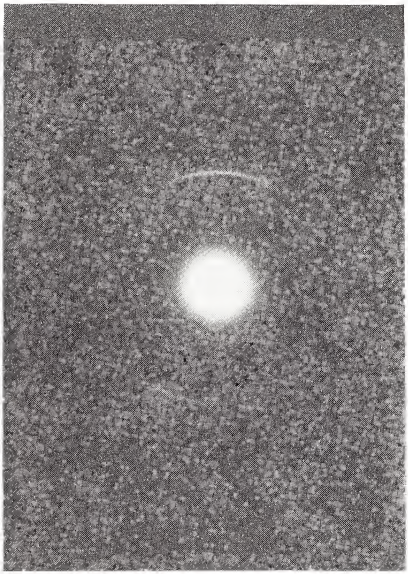

Fig. 4-A. Thin slice cut from paraffin sample prepared in electret apparatus. No field. X-rays normal to temperature gradient.

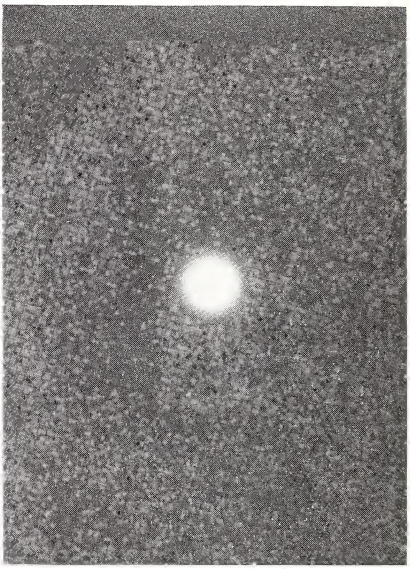

Fig. 4-B. Thin slice cut from paraffin sample prepared in electret apparatus. 30 KV-cm. Field X-rays normal to field and temperature gradient.

produces asterism as we observe it in the case of single crystals under mechanical stress.

From these experiments it is clear that the observed orientation is not an electrical phenomenon. Sometime ago Shearer and Mueller (6) found that paraffins solidified on a glass slide show definite orientation effects. This can be interpreted as similar to orientation of long chain molecules at interfaces as described by Langmuir and others. Our experiments show that only such an orientation can be observed, but no effect of an electric field. These results are in agreement with the conclusions reached from the piezo-electric experiments mentioned above.

Summary. X-ray investigations of paraffin, "electret" mixture, quartz powder suspended in solidified paraffin, and on sulphur have been carried out with the intention to determine the orientation effect of an

electric field during the solidification of the sample. In no case has any evidence of an effect of the electric field been found, and it is concluded that the orientation present is due to the temperature gradient and the effect of interfaces during solidification, but not due to the orientating action of the electric field on the molecules.

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THE HALL AND ALLIED EFFECTS IN CAST BISMUTH PLATES AS AFFECTED BY THE RATE OF COOLING

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While measuring the four transverse thermomagnetic and galvanomagnetic effects in a plate of bismuth cast from the molten metal certain abnormalities were noted in the results. As no published data could be found this research was undertaken to determine the effect of the rate of cooling of bismuth plates cast from the molten metal with respect to the four transverse effects and to help establish the relationship between heat and electricity.

The four transverse galvanomagnetic and thermomagnetic effects are shown schematically in figure 1, as they are most likely to be found

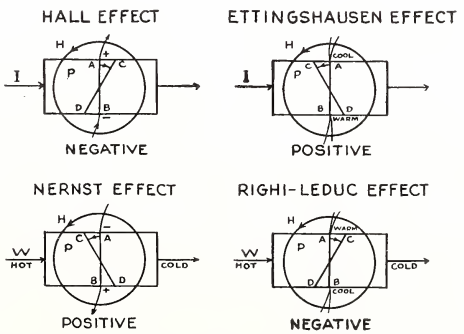

Fig. 1. Schematic diagram of the various effects.

in bismuth according to the convention of Campbell (1). The plate is represented by the rectangle P, I is the primary current, the circle H represents the magnetic field, the direction of the Amperian current in the electromagnet is given by the arrowhead. AB is an equipotential or equitemperature line, as the case may be, before the field H is on, CD is the position of this equipotential or equitemperature line, respectively, after the field is excited. If the direction of rotation of the line AB to the position of CD is opposed to the direction of the Amperian current H, as in the Hall and Righi-Leduc effects, the effect is negative. If the direction of rotation of the equipotential or equitemperature line AB to the position of CD is in the direction of the magnetic field H, as in Ettingshausen and Nernst effects, the effect is said to be positive.

A brass mold was used in casting the first two plates, but due to the difficulty in getting the bismuth loose from the brass sides was discarded for an aluminium mold. It was found that if the bismuth cooled slowly the plate appeared to be a single thin crystal with a definite cleavage plane almost parallel to the direction of expansion. Plates I and II were cooled in air and permitted to expand along the width of the plate. Plates III and IV cooled very slowly, expanding along the width and length respectively. Plate V was made by fast cooling brought about by pressing a piece of ice against each side of the heated mold and contents. This plate expanded along the width of the plate and had no definite cleavage plane. The crystals had random orientation and were reasonably large. Plate VI was made by placing the heated mold and contents in a solution of ice and ammonium chloride at -10° C. When the molten metal and mold were placed in the freezing mixture the bismuth shot out of the mold with explosive violence. It was found necessary to close the top of the mold before a satisfactory plate was obtained.

It is known that some gases have a greater solubility in iron, copper, and a few other metals when liquid than when solid. It was suspected that this explosive nature of bismuth, cooled quickly, was due to the rapid evolution of gases absorbed while molten. To determine the amount of this absorption about 3 cc. of bismuth were melted under the following conditions: in a vacuum, one-half atmospheric pressure and atmospheric pressure. If there were any gases absorbed in the molten state the quantity was so small that it was not detectable. Since bismuth expands 3.3 per cent in solidifying it seems to the writer that this rapid change in volume is a more plausible explanation of the explosive nature of bismuth.

Plate VII, of electrolytic bismuth, was furnished by Dr. F. C. Mathers of the Department of Chemistry.

The potentiometer method was used to measure the various effects. A flip coil and ballistic galvanometer was used to measure the field intensities. The thermocouples were copper, constantin of No. 40 B. & S. wire.

Fig. 2 shows a plot of the data taken for the Hall effect corrected for the Ettingshausen effect, which is superimposed on the Hall effect in the seven plates used. Field intensities H are plotted as ordinates.

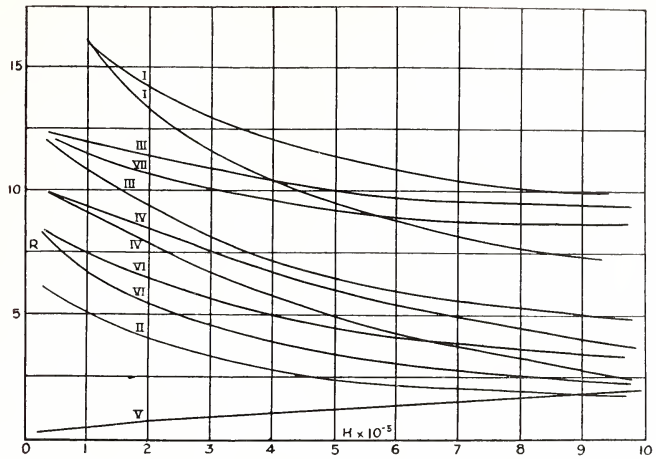

Fig. 2. Hall coefficient against Field Intensities.[1]

The Roman numerals above the curves indicate the plate for which the curve was drawn. Two curves having the same number indicate that the coefficient changed magnitude when the field was reversed. In taking data for these curves the plate was kept at room temperature and a current of 1.5 amperes was used. The Hall coefficient in Plate V was positive and increased as the field was increased. In all the other plates it was negative and decreased as the field was increased. No dissymmetry was found in Plate II, which was cooled in air, V, which was cooled quickly, and VII, which is electrolytic, i. e., the magnitude of the coefficient does not change when the field is reversed. Dissymmetry was

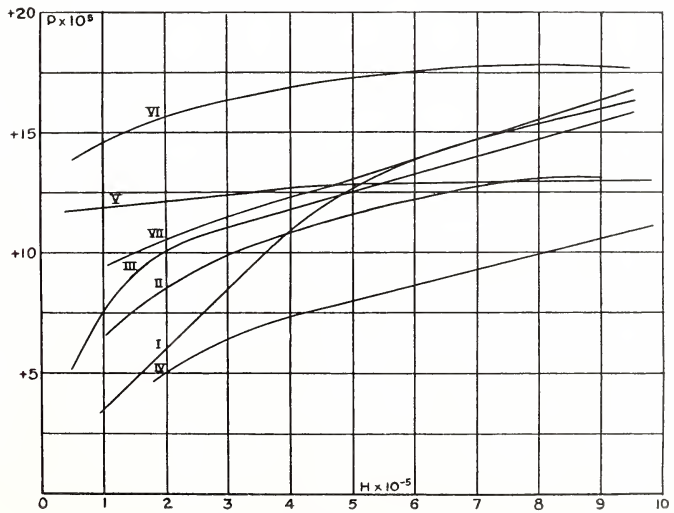

Fig. 3. Ettingshausen Coefficients against Field Intensities.[1]

[1] H x 10-5 should read, H x 10-3.

found in all the other plates when the field was reversed. Plate III, which was cooled slowly and had a very uniform crystalline structure, was found to exhibit the largest, while VI, formed by quenching, showed the smallest dissymmetry. Although Plates I and II were cooled under the same conditions the magnitude of the Hall coefficients of Plate II was approximately one-third the value for Plate I.

Fig. 3 shows the results of the data taken for the Ettingshausen effect. Field intensities are plotted as abscissae and Ettingshausen coefficient $P \times 10^5$ as ordinates. The plate was kept at room temperature and a current of 1.5 amperes was permitted to flow through the plate for at least two hours until a steady state was reached. The Ettingshausen temperature change took effect quickly at first and then more slowly, reaching a maximum after about a minute. From the graph it

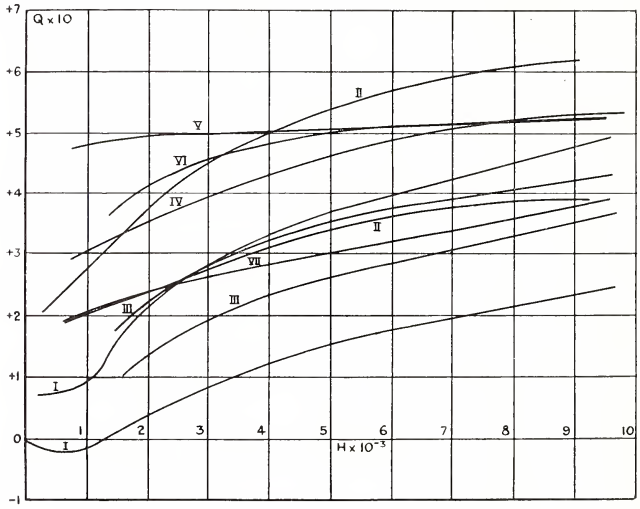

Fig. 4. Nernst Coefficients against Field Intensities.

is seen that the Ettingshausen coefficient increases with increase in field and tends to approach a limiting value. P for Plate VI shows a slight decline for high field intensities. Plates I, II, III, and IV were found to reach their limiting value more slowly than Plates V and VI, which were cooled quickly, and Plate VII, which is electrolytic.

Fig. 4 shows the results of the data for the Nernst effect corrected for the Righi-Leduc effect, which is superimposed on it. Field intensities H are plotted as abscissae and Nernst coefficients Q x 10 as ordinates.

In Plate I the Nernst coefficient was found to be negative with the field in one direction and positive with field reversed below 1300 gauss. Above 1300 gauss the coefficient was positive for either direction of the field. All the other plates were found to have a positive coefficient for all field intensities. A dissymmetry with reversal of the field was also found for the Plates IV, V, VI, and VII. The Nernst coefficient approaches a limit for high field intensities, but this limit is not the

same magnitude except for Plates IV, V, and VI, which were cooled quickly. It is concluded from these curves that fast cooling causes the Nernst coefficient to approach the same value at high field intensities. The coefficient in Plate VII, electrolytic bismuth, was found to be positive for all field intensities.

The results for the Righi-Leduc effect are shown in fig. 5. Field intensities H are plotted as abscissae and Righi-Leduc coefficients $S \times 10^6$ as ordinates. A large dissymmetry with direction of field was found for Plate I. With the field in one direction the coefficient is negative and decreased as the field was increased. When the field was reversed the coefficient was negative below and positive above a field intensity of 5200 gauss. A dissymmetry with reversal of field was found for Plate III. The coefficients were positive for low field in-

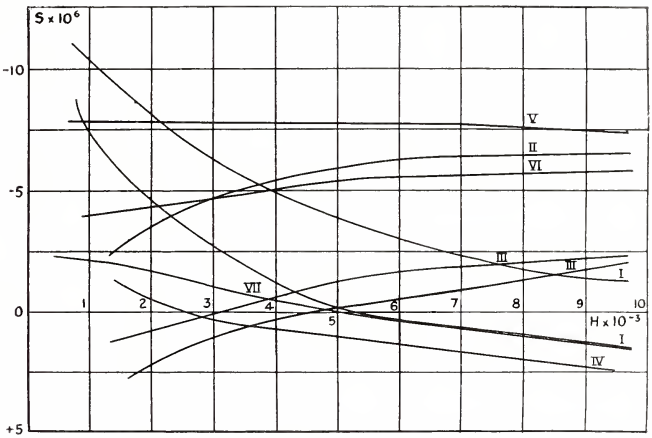

Fig. 5. Righi-Leduc Coefficients against Field Intensities.

tensities, but reversed at 3000 and 4700 gauss, respectively, and became negative as the field was increased. No dissymmetry with reversal of field was found for Plate IV, but the coefficient was negative below and positive above 2600 gauss. The coefficients of Plates V and VI are negative for all field intensities and no dissymmetry was found with reversal of field. No dissymmetry with reversal of the field was found for Plate VII, electrolytic bismuth, but the coefficient was negative below positive above field intensities of 5200 gauss.

In an effort to get some relation between the Hall, Ettingshausen, Nernst, and Righi-Leduc coefficients tables were made of the various values for each plate at 2000, 5000, and 9000 gauss from the curves shown in figures 2-5. According to Zahn (2), who extended Drude's (3) theory for the Hall and Allied effects, the ratios of the

$$\frac{\text{Hall coefficient}}{\text{Ettingshausen coefficient}} \quad \text{and} \quad \frac{\text{Nernst coefficient}}{\text{Righi-Leduc coefficient}}$$

should equal 2.5×10^4, and the sign of the ratio should be positive. When these ratios were calculated from the above mentioned tables of coeffi-

cients very little correlation was found between the magnitude and sign of the ratio.

The conclusion reached from this research are as follows:

1. The explosive nature of bismuth is not due to the absorption of gases when liquid, but is due to the sudden increase in volume on freezing.

2. The rate of cooling, size, and orientation of the crystals determined to a large extent the magnitude of the various coefficients.

3. There is very little correlation between the ratios of

$$\frac{\text{Hall coefficient}}{\text{Ettingshausen coefficient}} \quad \text{and} \quad \frac{\text{Nernst coefficient}}{\text{Righi-Leduc coefficient.}}$$

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CHARACTER OF THE ^3S TERMS IN THE MERCURY SPECTRUM

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On the basis of perturbation calculations in quantum mechanics and assuming the existence of more than one optical electron Langer[1] deduced an equation for the energy of the terms of spectra of complex atoms in the form of

$$\nu_n = \frac{R}{\left[n + \sum_{\circ}^{\alpha} \frac{p_{in}}{\nu_i - \nu_n}\right]^2} = \frac{R}{(n^*)^2}$$

where p_{in} is a function of the probability of transition between the terms ν_i and ν_n, and the ν_i is an observable spectroscopic term. This cannot be any term, but must arise from an electron configuration with nearly equivalent energy as that of one of the terms ν_n of the series. When no perturbing term ν_i is near enough to ν_n the formula reduces to the usual Ritz form and the plot of the quantum defect n*-n against ν_n is then a straight line. Where, however, the ν_i has a value falling amongst the terms of a series to which it does not belong then the plot of n*-n for that series should be similar to a dispersion curve around an absorption line.

Langer pointed out that such cases arise in the arc spectrum of mercury as well as other metals. A plot of the terms of the ^3S series determined from the 2^3P_2-m^3S lines was made by Shenstone and Russell[2]

from the wave-lengths published, and the value of n*-n was found to rise rapidly for the higher series members. This may sometimes be due to a wrong value assigned to the ground term and may be corrected by adding a small value to that term. In this case, however, no manipulation of the 2^3P_2 term could achieve a straight line plot for the ^3S terms.

At the suggestion of Dr. Shenstone a redetermination of the wave-lengths of this series was undertaken. The source consisted of a mercury arc in a quartz tube produced between a mercury cathode and an iron anode. The anode had a slot cut in it and through this slot mercury vapor passed from the arc into a low pressure chamber above, forming a beam of luminous vapor. The light from this beam, rich in the higher members of the mercury series, was analyzed by a Hilger E-1 quartz spectrograph. The lines from an iron arc superimposed on the Hg spectrum served for the comparison of wave-lengths. The accompanying table gives the wave-lengths and wave numbers of the 2^3P_2-m^3S series. The first eight lines are taken from Kayser's Handbuch, the next ten members being newly measured. In column 4 the term value is obtained by subtracting from $2^3P_2 = 40138.3$. These terms again have a large rise of n*-n for the higher series members, but when the 2^3P_2 is taken 2.5 units greater, viz., 40140.5, a straight line is obtained for the plot of n*-n against ν_n showing a Ritz relation, indicating an unperturbed series.

1 2^3P_2—m^3S m	*2* Wave Length	*3* Wave Number	*4* Term Value	*5* Corrected Term Value	*6* Residuals
2	5460.74	18307.5	21830.8	21833.3	+56.8
3	3341.48	29918.3	10220.0	10222.5	0
4	2925.41	34173.4	5964.9	5967.4	— 0.7
5	2759.70	36225.3	3913.0	3915.5	— 0.5
6	2674.99	37372.5	2765.8	2768.3	+ 0.7
7	2625.24	38080.7	2057.6	2060.1	— 0.2
8	2593.41	38548.0	1590.3	1592.8	— 0.1
9	2571.81	38871.6	1266.7	1269.2	— 0.4
10	2556.34	39106.7	1031.6	1034.1	0
11	2544.93	39282.0	856.3	858.8	— 0.3
12	.....	.....	.....	.....	.....
13	2529.47	39522.1	616.2	618.7	— 1.4
14	2524.12	39605.9	532.4	534.9	— 1.5
15	2519.81	39673.6	464.7	467.2	— 1.4
16	2516.26	39729.6	408.7	411.2	— 1.6
17	2513.32	39776.0	362.3	364.8	— 1.7
18	2510.86	39815.0	323.3	325.8	— 1.7
19	2508.70	39849.3	289.0	291.5	— 3.0

The equation then is

$$n^* - n = .30433 - 2.732 + 10^{-6}\nu$$

and the residuals for the observed term values minus the calculated term values are given in the last column. The large residual for the first term is quite a usual occurrence in spectral series.

PHYSICS TEACHING NOTES

THE PRODUCTION OF LIQUID OXYGEN AS A LECTURE TABLE DEMONSTRATION

A one-liter florence flask (round bottom) is prepared with a stem about 3 cm. in diameter and 20 cm. long. At the lower end is fused a small Dewar flask of about 4 cc. capacity. The liter flask with its stem is evacuated and filled to a pressure of 2.5 atmospheres with tank oxygen and sealed off. To produce *liquid* oxygen it is only necessary to submerge the stem with its small Dewar flask in liquid air. Almost immediately the gaseous oxygen will begin to condense in the cooled stem and trickle down into the small Dewar flask. After about one minute the stem is removed from the liquid air and it will be noticed that 2 or 3 cc. of liquid oxygen will have collected in the Dewar flask. The cold parts will soon be covered with frost. This may be removed by dipping the Dewar in a beaker of water for a few moments. The liquid oxygen is now visible and may be studied at leisure. It will last for a half hour or more.

The following simple calculation may be made: Volume of bulb and stem = 1150 cc. This volume was filled with O until the manometer read 96 cm. Hence total pressure = 96 + 74 = 170 cm. Therefore, the equivalent volume = 1150 × 2.3 atmospheres = 2600 cc. The manometer reading fell to 30 cm. when the stem cooled to the temperature of liquid air, i. e., to —180° C. Hence the volume liquefied

$$= 2600 \times \frac{140}{170} = 2100 \text{ cc.}$$

Now the density of liquid oxygen = .92, and that of the gas oxygen = .00142. Therefore, the volume of oxygen at N. P. T. required to produce 1 cc. of liquid is .92/.00142 = 643 cc. Hence the volume of liquid oxygen that the apparatus should yield when the stem is cooled to the temperature of liquid air is

$$\frac{2100}{643} = 3.3 \text{ cc.}$$

CHAS. T. KNIPP, University of Illinois.

A NEW LECTURE TABLE DEMONSTRATION TO SHOW THAT CATHODE RAYS LEAVE THE CATHODE NORMALLY

Ample proof is at hand experimentally and otherwise that cathode rays (electrons in motion) in a discharge tube leave the surface normally, and additional proof seems unnecessary.

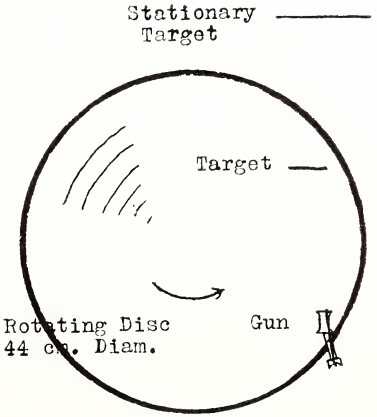
The following experiment is so simple and striking, yet on close observation is just what one would expect, that I venture a brief description of it. The apparatus may be blown by anyone handy with glass.

One of the electrodes in an ordinary discharge tube is in the form of a metallic cylinder (an aluminum tube about 2 cm. in diameter and 4 cm. long). Around this at equal intervals is placed single turns of, say, No. 20 nickel wire. The tube is now evacuated, primed with helium to make the cathode rays the more visible, and sealed off at a pressure giving a Crookes dark space of about 2 cm. and the cathode rays extending to the walls of the discharge tube. If now a discharge is passed through the tube with this electrode cathode the effect of the normality of the rays is at once visible. The rays fill the space out from the cylindrical cathode over its entire length, *except* where the single turns of wire are located. Each wire casts a shadow, yet the wire itself is a conductor! The explanation, obviously, is that the rays are radiated from the wire *perpendicular to its surface.*

Chas. T. Knipp, University of Illinois.

A ROTATOR ACCESSORY FOR SHOWING BY ANALOGY THE APPARENT DEFLECTION OF A PROJECTILE DUE TO THE ROTATION OF THE EARTH ON ITS AXIS

The following described rotator accessory may be used to demonstrate the fact that a projectile fired, for example, toward the east in the northern hemisphere seems to veer to the right. A small "bean shooter" made out of a spool and a wooden plunger was fastened on a rotator disc having a diameter of about 44 centimeters. The plunger of the gun was driven by a rubber band fitted to it. The gun was about 3 centimeters long. At a distance of 25 centimeters from the gun and at right angles to its bore a metal target was fixed in position on the rotator disc. Just back of this target a second target was mounted on a supporting stand. The target on the rotating disc was so placed that when the disc was stationary the bullet would just hit the outer edge of it. However, when the disc was rotated one revolu-



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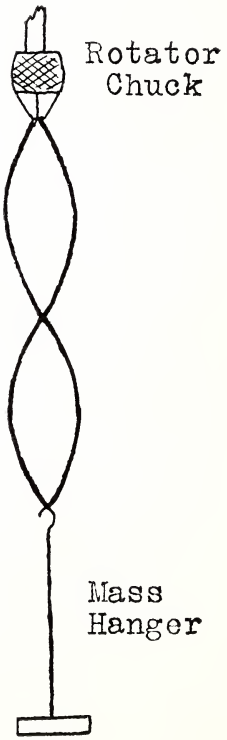
tion in two seconds, the bullet fired when its bore was at right angles to the plane of the stationary target would miss the target on the disc but would hit the stationary target. Thus while the bullet traveled from the muzzle of the gun to the rotating target, the latter moved to the left enough to cause the bullet to miss it and hit the stationary target. A coating of wax placed on the surfaces of the targets enables the observer to locate the position of the impact of the bullet. The accompanying diagram shows the arrangement of parts.

ROLLA V. COOK, Elwood.

THE FORMATION OF NODES AND LOOPS ON A WEIGHTED CORD BY MEANS OF A ROTATOR

The apparatus used in performing this simple experiment was as follows: A "chalk line" cord about two and one-half feet in length weighted at one end with an hundred gram mass-hanger had its other end clamped in the chuck of a rotator, the rotator shaft of which rotated about a vertical axis. By varying the speed of the rotator definite speeds were found at which the cord was made to break into one, two, three, etc., clearly defined loops having distinct nodes. The steadiness of these loops and nodes depended upon the steadiness and smoothness with which the rotator ran. Care was taken to keep the mass-hanger rotating about an axis along its stem rather than about some point in its stem as was its tendency to do. Perhaps less twisting of the cord would take place if a heavy braided cord like a heavy fish-line were used instead of a twisted cord. The accompanying diagram shows the arrangement of the apparatus.



ROLLA V. COOK, Elwood.

PAPERS FROM THE PROGRAM OF THE ZOOLOGY SECTION

INSECTS OF INDIANA FOR 1933[1]

J. J. DAVIS, Purdue University

The winter of 1932-33, following two successive mild winters, was only moderately severe and in most areas there was a covering of snow preceding the severest cold spells. As a result there was not the noticeable check on some insects as was anticipated. Mexican bean beetle, harlequin cabbage bug, corn earworm, and others, which are usually somewhat checked by winter conditions, continued to be more abundant north of their normal habitat.

As will be noted in Table I, the temperature was above normal during the mid-winter and summer months and the rainfall appreciably above normal in the early spring months but below normal during the summer months. This had a disastrous effect on some crops and proved highly favorable to many insects, such as codling moth, chinch bug, earworm and Oriental fruit worm.

CEREAL AND FORAGE CROP INSECTS

Chinch bug (*Blissus leucopterus* Say). This insect was more destructive in Indiana the past year than for at least 10 years. It was especially destructive in Benton, Newton, Lake, Porter and LaPorte counties in northwestern Indiana, and in Adams, Allen, Blackford, Elkhart, Jay, Steuben and Wells counties in northeastern Indiana. Of the small grains barley was especially heavily infested and apparently the source of the heaviest infestations. Summer conditions have been unusually favorable and the carry-over of bugs is probably the largest for over 40 years. With favorable conditions next spring we can anticipate great abundance of the chinch bug throughout the northern half of Indiana in 1934.

"Hessian Fly (*Phytophaga destructor* Say) has been at a low ebb throughout the year as a result of the very low carry-over from the fall of 1932, unusually high winter mortality, dry weather during the summer and early fall conditions unfavorable to fly activity. Infestations at harvest-time averaged only 7 per cent of the stems for the state as compared with 41 per cent in 1932. Summer mortality of aestivating puparia, due about equally to desiccation and parasitism, was unusually high, amounting to about 97 per cent in six northern and central localities where observations were made. On account of the

[1] This is the eighth report on the insects of Indiana, intended as an annual summary of the economic entomology of the state, and especially for use of future workers in the prediction of insect troubles. The writer is indebted to the following for records and information contained in this report: C. M. Packard, R. A. Sazama, W. B. Noble, B. J. Wilkins, G. A. Ficht, G. E. Marshall, G. E. Gould, V. R. Diamond and L. I. Musgrave.

low fly potentiality, and delay of wheat sowing, as well as fall fly activity as a result of the drouth, infestations this fall are likely to be very light."

"Wheat jointworm (*Harmolita tritici* Fitch). The harvest-time survey showed very low infestations over much of the state, but the average was brought up to 8 per cent of the stems by the unusual abundance of this insect in the north-central area. Here the average was 15 per cent and some really heavy infestations occurred in occasional fields."[2]

TABLE I. COMPARATIVE MONTHLY WEATHER DATA FOR INDIANA, 1933

Month		Temperature		Precipitation		Number of Days		
		State Mean °F	Departure from Normal °F	State Average Inches	Departure from Normal Inches	Clear	Partly Cloudy	Cloudy
January	Normal	29.0	.....	3.13	.....	10	7	14
	1933	38.6	+9.6	3.17	+0.04	11	7	13
February	Normal	30.5	.....	2.47	.....	9	7	12
	1933	31.4	+0.9	1.88	−0.59	14	7	7
March	Normal	40.5	.....	3.75	.....	10	8	13
	1933	40.1	−0.4	5.41	+1.66	8	8	15
April	Normal	51.9	.....	3.55	.....	11	9	10
	1933	51.8	−0.1	4.52	+0.97	10	9	11
May	Normal	62.1	.....	4.06	.....	12	10	9
	1933	65.0	+2.9	8.14	+4.08	9	11	11
June	Normal	71.4	.....	3.81	.....	14	10	6
	1933	77.2	+5.8	1.16	−2.65	23	6	1
July	Normal	75.4	.....	3.36	.....	16	10	5
	1933	77.0	+1.6	2.56	−0.80	18	9	4
August	Normal	73.2	.....	3.36	.....	15	10	6
	1933	72.8	−0.4	2.79	−0.57	17	9	5
September	Normal	67.2	.....	3.37	.....	15	8	7
	1933	72.4	+5.2	4.94	+1.57	14	7	9

European corn borer (*Pyrausta nubilalis* Hbn.) again experienced a very unfavorable season, the survival of larvae being the lowest since 1928, with the exception of 1930. Borers overwintered safely and early season conditions were favorable. However, during moth emergence and thereafter during oviposition and hatching of larvae the hot, dry weather was very unfavorable and, furthermore, most of the corn was small at the time of egg-laying and many of the egg masses that were laid peeled off as the corn plants showed the effect of the drought by a curling of the leaves. As a result there was not an appreciable increase in borer population, although in some fields where the corn was planted early and in regions not as severely affected by drought, the population increased very noticeably, again indicating the potentialities of this insect under normally favorable seasons. The extent of spread during 1933 was not determined as state and federal funds for this work have been discontinued.

The black or greasy cutworm (*Agrotis ypsilon* Rott.) was unusually abundant and destructive to corn in many sections of the state, thousands

[2] Statements in quotation by C. M. Packard.

of acres of corn being destroyed during June. Earliest reports were received the first of June and the last reports before the close of the month.

Webworms (Crambidae) were damaging corn at Rochester, June 27, the only report received during the year.

The common stalk borer (*Papaipema nebris* Gn.) was damaging corn at Vincennes, June 30, at which time they were quite small. No other reports, except a report of injury to potatoes at Milton, July 29, were received indicating that this stalk borer was not as abundant as usual.

Flea beetles (species unknown) were destructive to corn at Kempton, June 27.

White grubs (*Lachnosterna* spp.) were reported damaging lawns, corn and aster in a few localities in northern Indiana.

Alfalfa webworm (*Loxostege similalis* Gn.) destroyed alfalfa in a few northern Indiana localities the last of May and young alfalfa in several central Indiana localities the last week in September.

Clover leaf weevil (*Phytonomus punctata* Fab.) was abundant on alfalfa May 20, at Fairmont. Apparently much less abundant than normal.

Corn leaf aphis (*Aphis maidis* Fitch) was reported seriously damaging corn at Jeffersonville, August 19.

Wheat Midge (*Thecodiplosis mosellana* Gehin) was abundant in threshed wheat at Converse, August 12.

The carrot beetle (*Ligyrus gibbosus* DeG.) damaged sunflower grown for seed at Kendallville, August 10, by eating the underground parts.

VEGETABLE INSECTS

Harlequin cabbage bug (*Murgantia histrionica* Hahn) was destructive as far north as Austin but not as serious as in 1932.

Cabbage worms (*Pieris rapae* L. and *Autographa brassicae* Riley) were normally abundant.

Melon Aphis (*Aphis gossypii* Glov.) was unusually destructive to melons and cucumbers throughout the state during August. In the extensive melon section in the vicinity of Decker two-thirds of the melons were destroyed by this pest.

Onion thrips (*Thrips tabaci* Lind.) was more than usually destructive to onions in a number of localities in northern Indiana in July. The same species destroyed 30 acres of seedling carrots at Fort Wayne the last of July.

The flower thrips (*Frankliniella tritici* Fitch) caused the premature dropping of bean blossoms at Corydon in August.

Potato leaf-hopper (*Empoasca fabae* Harr.) was more than normally abundant and destructive in central and northern Indiana.

Potato flea-beetle (*Epitrix cucumeris* Harr.) was damaging potatoes at Kokomo early in July.

Mole cricket (*Gryllotolpa borealis* Burm.) was reported August 30, as damaging potatoes at Elkhart.

Tarnished plant bug (*Lygus pratensis* L.) was very destructive to late potatoes early in September at Kimmell and other points in northern Indiana.

Mexican bean beetle (*Epilachna corrupta* Muls.) was abundant throughout the state early in the season. The hot, dry conditions during mid-season reduced their numbers but they came back in abundance on the late beans. The potato beetle killer (*Perillus bioculatus*) was reported several times as commonly attacking Mexican bean beetle larvae.

Striped cucumber beetle (*Diabrotica vittata* Fab.) was somewhat more abundant than usual.

Corn earworm (*Heliothis obsoleta* Fab.) was unusually abundant and destructive to corn and tomatoes throughout the state.

Squash bugs (*Anasa tristis* DeG.) were very abundant in many sections of the state during July and August, attacking pumpkin, squash, melon and cucumber.

Other vegetable crop pests reported included cabbage aphid (*Aphis brassicae* L.), spotted cucumber beetle (*Diabrotica 12-punctata* Fab.), asparagus beetles (*Crioceris asparagi* L. and *C. duodecimpunctata* L.), Colorado potato beetle (*Leptinotarsa decemlineata* Say), squash vine borer (*Melittia satyriniformis* Hbn.) attacking squash and pumpkin in northern Indiana the first half of July, blister beetles (*Epicauta vittata* Fab., *E. pennsylvanica* DeG. and *E. marginata* Fab.) were destructive to potatoes, tomatoes and dahlias, white fly (*Aleyrodes vaporariorum* Westw.) was damaging greenhouse tomato and cucumber at Indianapolis, and the naked slug (*Limax* sp.) damaged lettuce the last of May at Anderson.

Strawberry leafroller (*Ancylis comptana* Fröhl.) was abundant in all parts of the state, especially in northern Indiana during July.

Turnip aphid (*Aphis pseudobrassicae* Davis) was very abundant on turnip in Northern Indiana the last of September.

FRUIT INSECTS

The codling moth (*Carpocapsa pomonella* L.) came through the winter of 1932-33 in large numbers and with favorable conditions during the season increased to enormous numbers, especially in the southern part of the state. Three full broods and a partial fourth occurred in southern Indiana. The following records of development were furnished by G. E. Marshall for Bedford. The first adult moth was taken in a packing house April 8 and the first moth was caught in an orchard bait trap May 11. First eggs were laid in field cages May 15 and hatched May 23. The larvae began to leave apples June 12 and the first moths of the second generation were observed June 22, the first eggs of this brood being laid June 29 and they were hatching July 3. The first third brood moths issued August 4 and they laid eggs August 8 which were hatching August 14. We have no definite records for the fourth brood worms.

Oriental fruit worm (*Laspeyresia molesta* Busck) was very abundant and destructive to late peaches and also to apples. In some cases peaches were 100 per cent infested.

Shot hole borer (*Scolytus rugulosis* Ratz.) was reported abundant attacking plum and cherry in several places in southern Indiana during August.

Rose chafer (*Macrodactylus subspinosus* Fab.) damaged apple fruits at Evansville, May 29.

Cherry slug (*Eriocampoides limacina* Retz.) defoliated cherry throughout the northern half of the state during July.

SHADE TREE AND SHRUB INSECTS

Orange-striped oak caterpillar (*Anisota senatoria* A. and S.) was reported as defoliating oaks at Kouts, September 7. Other reports without specimens for identification, indicated that this caterpillar was very prevalent throughout Northwestern Indiana.

Fall webworms (*Hyphantria cunea* Dru.) were common throughout the state, attacking wild and ornamental shrubs and trees, and unsprayed apples.

Bagworms (*Thyridopteryx ephemeraeformis* Haw.) were destructive farther north in the state than ever before, reports of defoliation of such trees as arbor vitae, blue spruce, and Lombardy poplar, being received as far north as Anderson and Lafayette.

Catalpa sphinx caterpillar (*Ceratomia catalpae* Boisd.) and ailanthus webworm (*Atteva aurea* Fitch) and the walnut worm (*Datana integerrima* G. & R.) were normally abundant, the last being much less abundant than in 1932.

Fall canker worm (*Alsophila pometaria* Harr.) was notably destructive to boxelder, maple, apple and plum at Shipshewana, May 29.

Boxelder bug (*Leptocoris trivittatus* Say) was annoying in homes throughout a greater part of the state during the past winter and spring months. The past summer and fall the species has reappeared in large numbers but apparently not as abundant as a year ago.

Oyster shell scale (*Lepidosaphes ulmi* L.) and pine leaf scale (*Chionaspis pinifoliae* Fitch) were abundant as usual, especially in the northern half of the state.

European elm scale (*Gossyparia spuria* Mod.) is apparently increasing and becoming a serious elm pest in the state.

Woolly maple aphid (*Phenococcus acericola* King) was abundant on hard maple at Jasper early in June.

Red spider (*Tetranychus telarius* L.) has been abundant and destructive as usual to evergreens and shrubs; also to phlox.

Elm cockscomb gall (*Colopha ulmicola* Fitch) and the maple bladder mite gall (*Phyllocoptes quadripes* Shim.) were normally abundant throughout the state.

Bronze birch borer (*Agrilus anxius* Gory) was responsible for the death of birch trees at Fort Wayne and Muncie.

Flat-headed borer (*Chrysobothris femorata* Oliv.) was a serious pest of hard and Norway maple throughout the state.

Mottled willow and poplar borer (*Cryptorhynchus lapathi* L.) was abundant in pussy willow and poplar throughout the northern half of the state.

Lilac borer (*Podosesia syringae* Harr.) was destructive to lilac at Crown Point during August.

FLOWER GARDEN AND ORNAMENTAL GREENHOUSE INSECTS

Rose scale (*Aulacaspis rosae* Bouché) and rose slug (*Caliroa aethiops* Fab.) were normally abundant.

Four-lined plant bug (*Poecilocapsus lineatus* Fab.) was destructive to mock orange and perennials at Anderson, June 9.

Lace bugs (*Corythucha marmorata* Uhl., Drake det.) were destructive to dahlia, aster and hardy scabiosa in several sections of the northern half of the state the last of July and during August.

Phlox plant bug (*Lopidea davisi* Knight) was destructive to phlox at Attica in September.

The Mexican mealy bug (*Phenococcus gossypii* T. and C.) was reported destructive to chrysanthemum at Bloomington the last of August.

Thrips (*T. tabaci* Lind.) were damaging chrysanthemum at Columbus and Lafayette the last of September.

Fern scales (*Hemichionaspis aspidistrae* Sign. and *Saissetia hemisphaerica* Targ.) were reported from many places during the year.

Wireworms (Elateridae) damaged chrysanthemums at South Bend the last of July, the infestation apparently coming in with a shipment of plants.

The wisteria leaf-tier (*Epargyreus tityrus* Fab.) was abundant at Hibbard, August 30.

MISCELLANEOUS INSECTS

The following household and annoying pests were reported from all parts of the state: ants, fleas, cockroaches, bedbugs, mosquitoes, silver fish, clothes moths, cigarette beetles, larder beetles, crickets and chiggers.

Termites (*Reticulitemes flavipes* Koll.) continue to cause immense losses throughout the state.

Eburia quadrigeminata was reported damaging cypress flooring at Shelbyville in May.

Powder post beetles (*Lyctus* sp.) were reported damaging house and barn timbers in all parts of the state.

Grain-infesting insects, including the rice weevil, saw-toothed grain beetle and cadelle, as well as the bean weevil were destructive throughout the state about the same as 1932.

The usual animal parasites, such as poultry lice, hog lice and ox warbles, were common in most sections of the state.

The cicada killer (*Specius speciosus* Drury) was apparently more than usually abundant judging from the number of reports received, oftentimes the report advising that they were annoying in lawns.

BEEKEEPING

Beekeeping is not only an important industry in Indiana for the products—honey and beeswax—which the bees produce, but also as an important aid in commercial fruit growing. The following notes on beekeeping conditions have been furnished by B. J. Wilkins, one of the State Apiary Inspectors. Bees came through the winter in comparatively good condition, ready to build up the colony strength sufficient to store a large crop of honey. Unfortunately drouth retarded the clover nectar

flow to such an extent that many colonies were on the verge of starvation during the summer months. Rainfall late in the summer resulted in a heavy flow of smartweed (heart's ease) nectar, enough in many cases to provide ample winter stores and in some cases a surplus was obtained.

State inspectors found but little European foulbrood but considerable sac brood and an enormous amount of American foul brood, the bulk being found in territory not worked by the inspectors for several years.

THE EFFECT OF LOWERED TEMPERATURE ON RETICULOCYTE FORMATION IN THE PIGEON

Dona Gayler Graam, Indiana State Teachers College

Introduction

While studying increased reticulocyte formation in pigeons, due to hemorrhagic stimulus, certain observations were made concerning reticulocyte formation in pigeons, due to the stimulus of decreased temperature of the environment.

Many workers (Wills, 1932), (Vaughn, Muller, and Zetzel, 1930) have mentioned the extreme sensitiveness of the blood manufacturing mechanism of the pigeon to many factors. Muller (1927) (1929 a and b) has reported the effects on reticulocyte formation in pigeons to certain articles of food. In an unpublished article, the present writer has reported the effect of hemorrhage on reticulocyte formation in relation to the length of life of the red corpuscle in both the rabbit and pigeon. In the present report the effect of cold on the reticulocyte formation, in pigeons, is presented.

Experimental Procedure. The results of this report are based on two planned experiments and two accidental observations. Two pigeons were purposely kept under uniform environmental conditions for nine months, then exposed to a rapid fall in the environmental temperature. Two accidental observations were made on two other pigeons, each of which at different times experienced a rapid fall in their environmental temperature.

In all four pigeons studied the reticulocyte count and environmental temperature were recorded. In case of pigeons of the planned experiments, the body temperature was also recorded over the entire experimental period and the reticulocyte count and body temperature were taken at the same time every day except the day the pigeons were exposed to cold; then their body temperatures were taken by way of the cloaca at one hour intervals for six consecutive hours. This article is a report of the results in the case of the two pigeons used in the planned experiments.

Staining Technique and Counting. I found the best method for staining the new red blood cells of the pigeon, referred to as reticulocytes in this paper, to be a modification of the method of Osgood and Wilhelm (1931) for the staining of human reticulocytes.

The staining solution consisted of 1 per cent aqueous solution (1 gr. —100 gr.) of Brilliant Cresyl Blue, .85 per cent NaCl and .3 per cent sodium citrate. Six drops of this solution were used to two or not more than three drops of the fresh blood. The mixture of blood and staining solution was shaken thoroughly and allowed to stand from 10 minutes to half an hour. The difference in time made no difference in the reticulocyte per cent, but if the mixture stood longer, the corpuscles began to disintegrate.

A droplet of the stained blood mixture was removed to a microscope slide, spread and allowed to dry. The red cells were examined immediately. The oil was dropped directly on the dried smear. If desired, the preparation can be kept for several weeks or months by mounting in balsam under a cover slip. However, the slide must be kept in the dark or it will soon fade. It is not necessary to counterstain.

Counting. Practically every red cell of the pigeon's blood contains some "basophilic" substance in the protoplasm. The younger cells contain the most of this so-called "basophilic" substance. One must learn to be consistent and he must arbitrarily decide which of these cells to call reticulocytes. I arbitrarily called those cells reticulocytes which had a complete chain of basophilic substance around the nucleus.

All those cells in one field of the microscope were counted (a micrometer disk was used to facilitate matters), the number set down and the field gone over a second time in order to count the reticulocytes. The slide was then moved to an adjacent field and the cells counted as above. Five hundred or more cells were counted in this way and then the percentage of new cells determined.

Food. Vaughn, Muller, and Zetzel (1930) found that after feeding pigeons a standard mixed grain diet for several weeks or even months, an established level of near 10 to 12 per cent of reticulocyte production was established. If this diet were modified by other substances such as meat or liver extract an immediate rise in reticulocyte manufacture was produced.

The pigeons used in all my experiments were grain-fed pigeons and the reticulocyte counts were extremely low and of great uniformity of number during the control periods.

RESULTS

Two pigeons, one of which is represented in figure 1 and the second in figure 2, were examined for reticulocyte percentage during a control period of five days immediately before they were placed outside in a tmperature 40°-50° F. colder than room temperature. The response of the two pigeons was very similar as can be seen in figure 1 and figure 2. The temperature of the room was fairly uniform during the control period at about 72° F. and the reticulocyte count varied only slightly at this temperature.

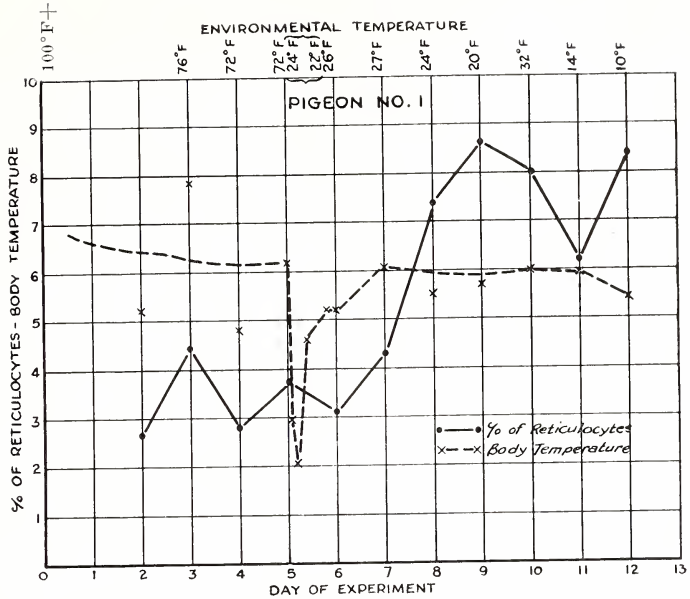


Fig. 1. The environmental temperature, the body temperature and the reticulocyte percentage were taken every day of the experiment and on the fifth day, after exposure to a fall in environmental temperature of between 40°-50° F., the body temperature was taken several times. The body temperature fell rapidly at this lower temperature, but after twenty-four hours the body temperature was back to normal. A reticulocyte peak was noted on the fourth day after the pigeon experienced the lower environmental temperature on the ninth day of the experiment. The reticulocyte response to cold continued from the eighth day to the end of the experiment on the twelfth day.

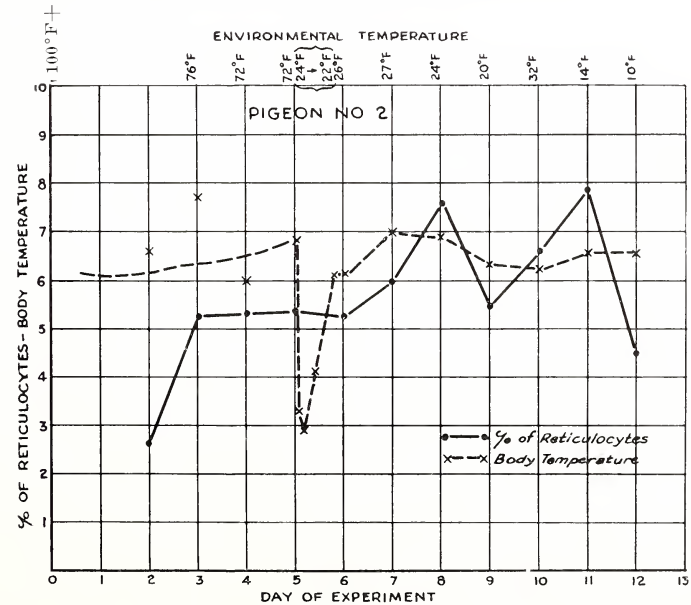


Fig. 2. Same explanation as for Figure 1 except the reticulocyte peak was reached on the third day after the pigeon experienced the lower environmental temperature or the 11th day of the experiment. The reticulocyte response to cold continued from the seventh day to the end of the experiment on the twelfth day.

On the fifth day of the experiment, the pigeons were placed in a colder temperature of 24° F. and the temperature remained at that level for the rest of the experiment. The body temperature of each was recorded every hour for six consecutive hours after exposure to cold and thereafter at intervals of twenty-four hours. It will be seen that there was a distinct fall of 4° or 5° F. in body temperature on exposure to cold in both cases but on the morning of the sixth day, twenty-four hours after exposure to cold, the body temperature had again reached normal or a matter of 105.3° F.; 106.1° F. respectively. From the sixth day on to the twelfth day, at which time the experiment ended, the temperature of the pigeons remained near this normal level. The reticulocyte count was still above that of the control period, on the twelfth day of the experiment. The reticulocyte percentage increased and reached a peak three to four days after exposure to cold and lowering of body temperature.

The reticulocyte response to hemorrhage which I have explained in an unpublished article and the reticulocyte response to cold are very similar, but if the cold produces an intravascular destruction of red corpuscles and so initiates the response in reticulocytes, I am not prepared to say.

CONCLUSIONS AND SUMMARY

1. Lowering the environmental temperature as much as 40° F. causes the body temperature of pigeons to fall a maximum of 4° F. in five hours.

2. The pigeons recovered their normal temperature of 105° F. in less than twenty-four hours.

3. A peak of reticulocyte formation occured on the fourth day (three days in some pigeons) after the pigeon's exposure to cold.

4. Presumably, the haemopoietic mechanism of the pigeon responded to a "cold" stimulus in a way similar to its response to a hemorrhage stimulus.

ACKNOWLEDGMENT

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CERTAIN FACTORS INFLUENCING THE RESPIRATORY METABOLISM OF THE LEECH (*Hirudo medicinalis*)

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While considerable data are available concerning the respiratory activity of invertebrates much is still found lacking regarding the annelids. In this group of animals reports have been limited to *Lumbricus*, *Nereis*, and *Hirudo*.

Thunberg (1905) reports an increase in oxygen consumption from 20 to 97 per cent atmospheric oxygen for *Lumbricus*. Konopacki (1907) finds no additional increase in oxygen consumption above 50 per cent oxygen, in earthworms. Dolk and Paauw (1929) record a constant rate of respiration down to ⅛th of the oxygen concentration of air, for earthworms. Amberson, Mayerson, and Scott (1924) find a dependence of oxygen consumption upon oxygen tension in *Nereis*. Hyman (1932) reports that no respiratory regulation exists in *Nereis* when the animals are placed in tubes resembling their natural habitat. Lindeman (1932) records an independence of oxygen consumption for *Hirudo* from normal saturation of water with air to about 20 per cent saturation.

Among the groups closely allied to the annelids should be mentioned the work of Henze (1910) which indicates a dependence of *Sipunculus* upon oxygen concentrations; and that of Hall (1931) on *Urechis*, an echiuroid worm, which states that oxygen consumption is independent of the oxygen pressure down to a value of 70 mm. Hg. (or approximately 50 per cent saturation). The latter author reports also that the oxygen pressure may drop from 115 to 4 mm. of Hg. in jars covered with oil.

Thus we see a uniformity apparently does not exist in the results of various workers with annelids and related forms.

Materials and Methods

The method of measuring the dissolved oxygen and the chamber in which the animals were kept were the same as used by Hiestand (1931) with the exception that the leeches were not confined to a cage within the jar but allowed complete freedom. The experiments included from four to nine animals.

For several tests the water was stirred by an electrically propelled paddle which was inserted through a hole in the rubber stopper. The speed of revolution, controlled by a system of reduction pulleys, was never great enough to molest the annelids, being about 75 turns per minute.

City tap water, aerated by bubbling air through it for several hours, was the respiratory medium. This aeration not only expelled the free carbon dioxide with which the water was well saturated, but also brought

the oxygen content to equilibrium with atmospheric air. Since there was a possibility that a certain amount of the oxygen consumption attributed to the leech might have been caused by microorganisms present, tests, varying in length from three to forty-four hours, were made to establish certainty on this subject. In all cases there was no appreciable decrease in oxygen tension. This not only dismissed the possibility of tension reduction by bacteria but also established the efficiency of the method of sealing the respiration chamber.

The animals were permitted to remain undisturbed in an open jar for a week, a time sufficient for laboratory acclimatization. They were not fed until before the last series of experiments. During starvation the animals were found to lose weight at a comparatively rapid rate. Over a period of 39 days the weight loss was approximately 4.3 grams compared to a previous total weight of 13.610 grams. This diminution in weight was due to catabolic changes within the leeches and hence did not have any abnormal effects on the respiration rate.

The effect of food on the rate was reserved as the last experiment. The leeches were placed on the inner surface of a rabbit's ear and permitted to engorge themselves until satisfied.

Throughout the experiment uniform standard conditions were closely adhered to. The tests were carried out in an isolated room where the temperature was 23° C. with variations less than 1°. A small electric light bulb supplied a constant light during the experiments and in intermediate periods. Approximately 11 ml. samples of water were withdrawn at each sampling. Of this 10 ml. were used for oxygen determination.

It was found that tap water formed a natural environment for the leeches. Distilled water could not be used since prolonged confinement in it caused several leeches to die. Also a considerable quantity of mucous secretion was exuded by the animals in distilled water. Possibly this was due to the osmotic pressure difference between the leech and the water.

RESULTS

Normal Respiration Rate. In the first series of experiments 6 leeches having a total weight of 13.672 grams were used. A series of tests was carried out to determine the average respiration rate in water, the oxygen tension of which was reduced by the respiration of the animals themselves. At the start of the experiment the jar contained approximately 950 ml. of water. Determinations were made usually at two hour intervals until 10 hours had elapsed. An average result is shown in Table I. It was noted in these first and later experiments that when successive determinations were made on successive days, the *rate of oxygen consumption diminished slightly during the successive trials* (see Tables II and III); in other words the leeches responded by "acclimatization" and their metabolism diminished somewhat. If a few days elapsed in which time the animals were not subjected to low oxygen tensions, their respiration rate returned to normal.

Table I (normal)

Hrs.	Mgr. O_2 per liter
0	9.10
3	5.88
6	3.76
8	2.84
10	2.04

Table II

Hrs.	Mgr. O_2 per liter
0	8.90
2	7.00
4	5.20
6	4.76
8	3.84
10	3.24

Table III

Hrs.	Mgr. O_2 per liter
0	8.50
2	7.04
4	5.90
7	4.68
9	4.08

Table IV (high oxygen)

Hrs.	Mgr. O_2 per liter
0	25.04
3	21.64
6	19.28
8	15.68
24	3.64
26	2.20
27	1.68
28	1.40
29	1.24
30	1.08
31	1.04
32	.90

Table V (high oxygen plus high carbon dioxide)

Hrs.	Mgr. O_2 per liter
0	25.80
3	22.60
6	18.36
8	16.84
11	14.24
24	3.32
26	1.96
27	1.60
28	1.36
29	1.28
30	1.00
31	.86
32	.76

Table VI

Hrs.	Previous to feeding Mgr. O_2/L.	1st day following Mgr. O_2/L.	2nd day following Mgr. O_2/L.	3rd day following Mgr. O_2/L.	4th day following Mgr. O_2/L.
0	10.20	10.30	10.40	10.30	10.36
3	7.12	5.02	4.90	6.70	6.24
6	4.34	2.64	2.44	3.70	3.76
9	2.80	1.90	2.14	2.64	2.40

Effects of High Oxygen Tensions. Since it was determined by the preceding tests that oxygen consumption decreased at low oxygen tensions it was thought advisable to determine if higher oxygen tensions than normal air-water equilibrium would accellerate respiration. Tap-water which had been washed free of dissolved carbon dioxide was shaken with oxygen from a supply tank until it contained 25.04 mgr. oxygen per liter. The same six individuals were placed in this super-

saturated water and samples were taken for a period of 8 hours. On the following morning the experiment was continued, the leeches being left in the chamber over night. Samples were taken until a total period of 32 hours had elapsed. The results are indicated in Table IV. It can readily be seen that the oxygen consumption took place at a greater rate at very high oxygen tensions than at normal saturation. When a tension of 2.20 mgr. per liter was reached the respiration rate was considerably reduced. At the conclusion of this experiment the question was raised as to the effect of combined high oxygen and carbon dioxide.

Effects of High Oxygen and High Carbon Dioxide. Tap water was mixed with oxygen and carbon dioxide from tanks until the oxygen content was raised to 25.80 mgr. per liter and the carbon dioxide content increased to 489.5 mgr. per liter. The same procedure as in the preceding experiment was followed. The results are recorded in Table V. It will be noted that the results are practically identical with those of high oxygen content alone. The differences are so slight as to be considered more or less insignificant.

Since respiration had practically ceased at the end of the two preceding tests it was questioned if the animals actually formed an oxygen debt.

Determination if Leeches Can Form an Oxygen Debt. The procedure followed was that of confining the animals for a period of 15 hours in the respiration chamber, determining the oxygen tension of the water at the end of this period, and immediately transferring the leeches to normal stock water, the oxygen tension of which was known. Then in the following eight hour period, with determinations made regularly at 2 hour intervals any increased oxygen consumption of the leeches (which would indicate a debt) could be ascertained.

Two such determinations were made, the data of which are not included in this paper. The results, however, show a slight acceleration in respiration for the first 2 hours in the fresh stock water after a previous period of low tension, but at the end of the 8 hour period no more oxygen was consumed than normally. We do not believe this evidence as being indicative of an oxygen debt formation. In all probability the return to water of normal oxygen tension from that of low tension acted as a mild stimulation to the respiration of the leeches, but the resultant accelleration soon diminished and at the end of a given period (8 hours) approximately the same volume of oxygen was consumed as in the normal tests, which fact would indicate the absence of an oxygen debt formation.

Effect of Circulation of Water on Respiration. In a previous paper one of us (Hiestand, 1931) demonstrated the effect of volume of water on the rate of oxygen consumption of the crayfish, *Cambarus virilis*. He found that whether this species could be said to be dependent upon or independent of oxygen tension of the surrounding water, involved not only the gaseous tension of the water but also the volume of the water, i.e., total quantity of oxygen available. Thus the possibility that water in motion might influence the oxygen consumption presented itself. For investigating this possibility, the circulating device previously described

was built. Four determinations with normal stock water were made and compared with the normals in quiet water of the same stock.

The results showed no appreciable change in the rate of consumption, the only visible difference being in the behavior of the leeches. They did not remain as motionless as in still water but often set up an undulating motion which indicated their sensibility to the water in motion. The same type of undulating motion was apparent also when leeches were transferred from low tension water to higher. It is apparently a reaction brought about by the stimulation of water of high oxygen content as well as by circulation of water for it occurred in water supersaturated with oxygen. It was also noted that, although the water was kept in motion, the leeches could not respire at lower tensions than in quiet water.

Effect of Ingestion of Blood on Respiration Rate. Five leeches whose normal respiration rate had been determined were fed by being placed upon the inner surface of the ears of a live rabbit. After they had become gorged with blood they were weighed. Their gain in weight is shown by the following table:

Total weight previous to feeding	7.726 gms.
Total weight after feeding	23.574 gms.
Weight of blood ingested	15.848 gms.

On the following four days oxygen determinations were made as comparisons with those before feeding. In each case an increase in oxygen consumption above that of inanition occurred, being most marked during the second day following feeding. At the end of a six hour period in the animal chamber the oxygen consumption showed about a 30 per cent increase after feeding above that of a similar period during inanition. The increase was less marked in the remaining three hours of the test. The results are shown in Table VI.

Discussion

The authors have been aware of two facts throughout this work. One is the fact that slight variations occur from time to time under supposedly identical conditions. This is to be expected when one deals with living forms, however, and is experienced by all who come in contact with problems of respiratory metabolism. The other fact is the acclimatization that occurs among the animals. As has been stated earlier in this paper, leeches show an adjustment to conditions, such that if successive tests are conducted on successive days, the oxygen consumption will diminish slightly as the animals become adapted to the lowering tensions. This, in itself, is an important fact, for it is one means of regulation that the animals possess.

In his paper, Lindeman (1932) shows graphically a "straight-line" relationship between oxygen tension and oxygen consumption until low tensions are reached. Our results do not quite agree. As the tension diminishes the consumption gradually recedes but this recession becomes much more marked at tensions less than 2 mgr. O_2 per liter. Thus we cannot say that an actual dependence exists except at tensions above

normal equilibrium of air and water. We feel safe in saying, however, that the animals are virtually independent over most of the range below normal air and water equilibrium. Above normal saturation a complete independence exists. This is not surprising, when one considers that the leech lives in an external environment where the water is relatively rich in oxygen most of the time.

Also we do not find that removal of a small amount of water by sampling affects the respiration of the leeches. Our method does not involve replacing the water withdrawn and therefore little disturbance occurs within the jar.

CONCLUSIONS

1. Oxygen consumption of *Hirudo medicinalis* is independent of oxygen concentration above normal air and water equilibrium.
2. As the tension of oxygen is reduced from normal air and water equilibrium by the respiration of the leeches, the oxygen consumption rate gradually decreases until a tension of about 2.0 mgr. per liter is reached. Below this value respiration decreases gradually and ceases at about .80 mgr. per liter which is approximately 1/10th that of normal air-water equilibrium.
3. Oxygen saturation above normal air-water equilibrium accellerates respiration but throughout this range the oxygen consumption is quite uniform.
4. Water rich in CO_2 as well as O_2 does not increase the rate above that of water rich in O_2 alone.
5. No evidence that the leeches can form an oxygen debt was found.
6. Circulating water does not materially affect the O_2 consumption.
7. Ingestion of blood increases the rate of O_2 consumption markedly.

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RECORDS OF INDIANA DRAGONFLIES—VII. 1932-1933

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This is the eighth of a series of papers,[1] giving additions to the state list of species of Odonata, new county records, or captures of rare species already known from Indiana and important and interesting ecological or descriptive notes on the species concerned, since Williamson's annotated list of 1917.[2]

The present paper contains not only records from 1932 and 1933 but also many from specimens collected in former years—some of them as long ago as 1905—which were laid aside for later study because they could not be identified. Most of these were females of species of which both sexes had not been adequately described or associated. The gradual accumulation of material, including mating pairs, and the preparation of generic revisions in the meantime have made it possible to positively identify almost all of this material now. Two species not previously recorded from the state (*starred in the list of species) are listed, making a total of 135 species known from Indiana.

More than 2500 specimens, representing 90 species, were included in the collections studied for this paper. This material included all specimens of Odonata collected in Indiana by Mr. E. B. Williamson and his associates in 1932 (340 to 370), and by Esther Barrett Montgomery and the author in 1932 and 1933 (3219 to 3375). In addition to these rather large lots of specimens, there were available for study several small collections, including a few specimens from Zionsville and Indianapolis furnished by R. A. Ragains, a small collection made in Delaware County in 1931 by W. B. Ely and furnished without further data, collections from Mishawaka made by A. W. Trippel (11), from Lake Maxinkuckee by Howard North and M. K. Williamson many years ago but undated, from Morgan County by L. I. Musgrave (10), from Kosciusko County by G. E. Gould, from St. Joseph and other counties by G. Walker Daubenspeck (1-4), and specimens collected at Lafayette and Henryville by students of Purdue University as a part of their class work (P. U.).

Mr. E. B. Williamson furnished the following general notes on his collecting activities in 1932.

"In 1932 E. B. Williamson was assisted in collecting in Indiana by R. G. Blodgett, Eli Captain, Miss Margaret Ann Clippinger, Mark Decker, Mr. and Mrs. W. H. Ditzler, Mrs. H. K. Gloyd, K. M. Kunkel, Nathan Linn, Dr. Z. E. Malcolm, J. Ross McCulloch, Dr. Lyman T. Rawles, Mr. and Mrs. Norman Shufelt, Misses Mary and Jane Williamson.

"At the Monument City bog in Huntington County on June 12, Eli Captain and I saw two females of *Tachopteryx thoreyi* each ovipositing in a scant cup full of water. Mr. Captain saw a *thoreyi* catch a *Caloptery x maculata.*

[1] Proc. Ind. Acad. Sci., **29**:99; **34**:383; **36**:287; **38**:335; **39**:304; **40**:347; **41**:449.

[2] Uni. Mich., Mus. Zool., Misc. Publ. No. 2, 1917.

"At Vanemon's Swamp on June 28, Norman Shufelt and I saw two or three males of *Aeshna mutata* ranging widely over the extensive and increasing spatter-dock beds, and much bothered by the numerous and irritating males of *Neotetrum pulchellum*. The same day we went to Chalfant's gravel pit where many females of several species of Enallagma and of *Ischnura verticalis* were ovipositing, the Enallagmas always accompanied by males, the Ischnuras always alone. Males of *I. verticalis* are devoid of gallantry under every circumstance and several times I have seen them deliberately knock resting females from their perches.

"On June 30 I saw a male *Nasiaeschna pentacantha* flying a short beat on Pigeon River. At the time many bits of willow cotton were falling into the river, and the dragonfly, apparently in a spirit of play, attacked many of these, dispersing them, like an explosion into smaller fragments. The legs, well trained in the capture of prey, made short work of the slowly drifting bits of cotton. Later the dragonfly flew around a bend in the river, and almost at once, from the direction in which it had disappeared, a male *Hagenius brevistylus* high in the air, flew over my head. It was struggling with a large dragonfly which I thought at first was a female of its own species, but I soon saw that this was not the case. It flew to the top of a tall willow which overhung the river, selecting a perch indiscernible to me. I waded to a point in the river as nearly as possible under its assumed position and in a few seconds the head of a male *N. pentacantha* plumped in the water near me. I watched for wings, but saw none—probably the wind carried them to a distance. Later in the day, I saw a female *H. brevistylus* ovipositing, and every drop of water she threw with her abdomen fell on the river bank, in close proximity to the water—but always on the bank.

"On July 24 there were no *Enallagma divagans* or *exsulans* among the lizard-tail through which Flat Creek has a narrow channel and where the species were common in 1930."

In order to present the data within as small a space as possible, collector's numbers, referred to above, are listed here with the locality, date and such other details (including quotations from field notes) as seem desirable, and these numbers with the county only instead of the complete data are quoted in the list of species.

1. Boy Scout Camp, South Bend, June 13, 1932.
2. Stream and swamp nine miles west of Connersville.
3. Lake at Lakeville, June 13, 1932.
4. "Old gravel pit, small pond, about five miles north of Rochester, east side of Road 31. Noon. Sunny. Very dense dragonfly population," June 13, 1932.
10. Pond and stream, Green Township, Morgan County.
11. St. Joseph River at Mishawaka.
340. Monument City bog, 9 a. m. to 3 p. m., June 12, 1932.
341. Salamonie River, Monument City, June 12, 1932.
344. Case Lake (Lane Lake), east of Howe, June 17, 1932.
345. Pigeon River, near Road 9, Howe, June 17, 1932.
346. Same locality as 345, June 18, 1932.
348. Pigeon River, below Howe, June 22, 1932.

349. Eel River, near Hoover, June 26, 1932.

350. Twelve Mile Creek, west of Hoover, June 26, 1932.

351. Mud Creek, west of Hoover, June 26, 1932.

352. Vanemon Swamp near Bluffton, June 28, 1932.

354. Pigeon River below Howe, June 30, 1932.

356. Flat Creek in Wells County, near Huntington County line, July 9, 1932. "The creek was still in flood from heavy rain July 7, and two or three times its normal width. Two or three *Neotetrum pulchellum* and several *Calopteryx maculata* were seen. Somatochloras were apparently still flustered and disturbed by abnormal condition of the stream. They followed the stream a short distance, then breezed away over the field; the females seemed bewildered by the lack of suitable places to oviposit."

357. Creek in woods, west of Markle, July 10, 1932.

359. Same as locality 356, July 10, 1932. "About 4-5 p. m. Creek still swollen to about twice its normal size. Flight of Somatochlora was wild and irregular."

360. Lake Garrett (Franz Fish Pond), Liberty Center, July 11, 1932.

362. Same as locality 360, July 13, 1932.

363. Same as locality 356 and 359, July 14, 1932. "Day cloudless, maximum temperature 94° F.; previous night hot, making today a good Somatochlora day. Arrived at creek about 7:00 a. m.; Somatochloras very active at time of arrival. Left creek at 11:30 a. m.; by that time both species were doing a lot of hanging up—*ensigera* on immediate creek bank on bluegrass and very slender weeds, *linearis* on dead twigs of bushes overhanging creek, at height of two to ten feet, usually between four and eight feet. Never saw *ensigera* hang up before—believe it was due to excessive heat. At a large pool in full sun in creek (pool 1-15 x 30-40 feet) took *linearis* patrolling pool exactly like a Macromia or *Epicordulia princeps*. A mating pair of *ensigera* taken in grass along creek. As observed before Somatochloras seem to catch only small insects."

364. Creek near Murray, July 15, 1932.

367. Flat Creek, same locality as above, July 24, 1932. "Cloudy, but no wind. Arrived at creek about 3:30 p.m., and stayed until 5:30 p.m. As to be expected because of clouds and time of day few Somatochloras were seen. Creek has almost ceased to flow—water yellow-green with algal bloom."

368. Flat Creek, same locality as above, July 31, 1932. "Only three or four Somatochloras seen. Creek has ceased to flow."

370. Lake Garrett (same as 360 and 362), July 31, 1932.

3219. Wild Cat Creek, about three miles east of Lafayette, July 4, 1932. At this point the creek flows within vertical clay banks, six to ten feet high. Within the stream bed, however, there are gravel and sand bars, partly bare and partly overgrown by willows, shallow and deep flowing water and extensive pools of still water.

3220. Freeman Lake, a few miles south of Monticello, August 3, 1932.

3316. State Forest, at Henryville, June 12-14, 1933. "A few Somatochloras were seen—one was seen hawking along a water course in the early afternoon. I threw small stones into the air as it came toward me; it followed one of the falling stones almost to the ground, being only three or four inches above it when it struck the ground."

3357. Wild Cat Creek, same locality as 3219, August 20, 1933.

3361. Sugar Creek at Crawfordsville, August 30, 1933.

3363. Birch Creek near Prairie City, August 30, 1933.

3364. Pond at Howesville, August 30, 1933. "A long, narrow pond—formerly a stream bed—with a good growth of yellow and white water lilies in the water and smartweeds, grass, etc., along the margin. The sun was not shining and few dragonflies were seen."

3365. Dredged ditch, six miles south of Linton, on Road 59, August 30, 1933. "The water was about knee deep at the bridge, but there was no current, and this was apparently only a long pool in an otherwise dry stream bed. The margins and little islands here and there were grown up with grass."

3366. Old water supply lake, Oakland City, Aug. 31, 1933. "I spent about two hours (2:45-4:30 p. m.) at the old lake. A complete circuit of the lake was made. Lestes, almost all females of *rectangularis*, *Anomalagrion hastatum*, mostly tenerals, and *Erythemis simplicicollis* were present in great numbers."

3367. New water supply reservoir, Oakland City, Aug. 31, 1933.

3368. Lake, formerly water supply reservoir now turned into park for swimming, Boonville, Sept. 1, 1933. "Only a small portion of the shore line is devoted to the bathing beach, the greater part is grown up with the cat-tails and plants of similar habitat; in places the ground is marshy for some distance back from the shore line. Dragonflies numerous in both species and individuals."

3369. Water supply reservoir, Boonville, Sept. 1, 1933.

3370. Pool along Road 62 about three miles south of Dale, Sept. 1, 1933. A ditch along the road contained a pool of muddy water a few feet wide and from a few inches to a foot in depth, extending for almost a half mile.

3371. Water supply lakes, Huntingburg, Sept. 1, 1933.

3373. Little Pine Creek, east of Independence, Sept. 17, 1933.

3374. Kate's Pond, northwest of Independence, Sept. 17, 1933.

3375. Pine Creek, near Templeton, Sept. 17, 1933.

List of Species

3.[3] *Agrion maculatum* Beauvais. **Clark**[4] (3316); **Huntington** (357); **Marion**, Indianapolis, June 25, 1930; **St. Joseph** (11), July 11.

4. *Hetaerina americana* Fabricius. **Benton** (3375).

6. *Lestes congener* Hagen. **Lagrange**, Mt. Pisgah, Sept. 4, 1928.

11. *Lestes rectangularis* Say. **Fayette** (2); **Lake**, dry marsh, three miles east of Merrillville, Aug. 12, 1931 (Daubenspeck).

13. *Lestes unguiculatus* Hagen. **Gibson**, old lake, Oakland City, July 28, 1929; **Posey**, pond north of Poseyville, July 4, 1924.

[3] The numbers of Williamson's 1917 list are used.

[4] Names in bold face refer to counties.

15. *Argia apicalis* Say. **Clay** (3363); **Dubois** (3371); **Marshall,** Lake Maxinkuckee; **Spencer** (3370) **Tippecanoe** (3357).

16. *Argia moesta* Hagen. **Tippecanoe** (3219).

17. *Argia sedula* Hagen. **Benton** (3375); **Montgomery** (3361) **Tippecanoe** (3357).

18. *Argia tibialis* Rambur. **Lagrange** (348, 354); **Sullivan,** Busseron Creek, near Paxton, July 15, 1928; **Tippecanoe** (3219, 3357).

20. *Argia violacea* Hagen. **Clay** (3363); **Greene** (3365); **Huntington** (357); **Marshall,** Lake Maxinkuckee; **Tippecanoe** (3219); **Warrick** (3368).

22. *Enallagma aspersum* Hagen. **Fountain,** Veedersburg, June 4, 1905 (Deam).

22a. *Enallagma basidens* Calvert. **Dubois** (3371) 2 ♀; **Gibson,** water supply reservoir, Oakland City, July 1, 1930, and June 14, 1931, one female each date, (3366) 3 ♂ 4 ♀, (3367) 29 ♂ 14 ♀; **Greene** (3365) 5 ♀; **Knox,** gravel pit, Emison, Aug. 9, 1929, 1 ♂ 1 ♀; **Lawrence,** stream, near Bedford, Aug. 18, 1931, 1 ♂; **Vigo,** pond three miles south of Pimento, July 4, 1929, 1 ♂; **Warrick** (3368) 30 ♂ 24 ♀, (3369) 9 ♂ 7 ♀; **Wells** (360) 13 ♂ 8 ♀, (362) 10 ♂ 4 ♀, (370) 7 ♂ 2 ♀. The occurrence of this species in increasing numbers since its discovery in the state in 1929, indicates that it has probably spread into our territory only recently.

25. *Enallagma civile* Hagen. **Dubois** (3371); **Spencer** (3370); **Warrick** (3368, 3369).

28. *Enallagma ebrium* Hagen. **Kosciusko,** Webster Lake, May 29, 1932 (Gould); **St. Joseph** (3).

29. *Enallagma exsulans* Hagen. **Greene** (3365); **Montgomery** (3361); **Spencer** (3370); **St. Joseph** (11) June 15 and July 25, 1932; **Tippecanoe** (3219, 3357).

33. *Enallagma vesperum* Calvert. **Laporte,** pond, June 11, 1932 (Trippel); **St. Joseph** (11), July 12, 1932, (3).

34. *Enallagma signatum* Hagen. **Dubois** (3371); **Spencer** (3370); **Warrick** (3369); **White** (3220).

36. *Nehalennia gracilis* Morse. **Miami** (351), 3 ♂ 1 ♀.

38. *Amphiagrion saucuim* Burmeister. **Delaware** (Ely); **Miami** (351).

41. *Ischnura posita* Hagen. **Clay** (3364); **Dubois** (3371); **Spencer** (3370); **Warren** (3374); **Warrick** (3368).

43. *Ischnura verticalis* Say. **Benton** (3375); **Clay** (3363, 3364); **Dubois** (3371); **Greene** (3365); **Spencer** (3370); **Warren** (3373, 3374); **Warrick** (3368, 3369).

45. *Tachopteryx thoreyi* Hagen. **Huntington** (340), 10 ♂ 2 ♀.

46. *Cordulegaster diastatops* Selys. **Huntington** (340), 3 ♂.

49. *Progomphus obscurus* Rambur. **Cass** (350) 2 ♂.

50. *Hagenius brevistylus* Selys. **Lagrange** (348) 3 ♂ 4 ♀, (354) 6 ♂ 3 ♀.

51. *Ophiogomphus rupinsulensis* Walsh. **Lagrange** (346) 1 ♂ 1 ♀, (348) 1 ♂ 1 ♀, (354) 2 ♂.

*52b. *Gomphus cornutus* Tough. **Fulton** (4) 1 ♂. Although Mr. Williamson quoted the original description of this species in the Pro-

ceedings of this Academy for 1900 with the statement, "This species will very probably be found to inhabit Indiana," it had not been taken within the state until Mr. Daubenspeck, who has collected several specimens of it in northern Illinois and southern Wisconsin for me, captured the specimen here recorded, last year.

54. *Gomphus lineatifrons* Calvert. **Lagrange** (345) 3 ♂, (346) 27 ♂ 3 ♀, (348) 31 ♂ 11 ♀, (354) 2 ♂ 6 ♀.

55. *Gomphus exilis* Selys. **Lagrange** (344) 1 ♂.

56. *Gomphus fraternus* Say. **Huntington** (341) 2 ♂; **Lagrange** (346) 3 ♂ 3 ♀, (348) 4 ♂ 1 ♀, (354) 3 ♂ 1 ♀.

58. *Gomphus graslinellus* Walsh. **Cass** (350) 8 ♂ 1 ♀; **Wells** (352) 1 ♀, (360) 1 ♀.

59. *Gomphus lividus* Selys. **Cass** (350) 2 ♂ 2 ♀; **Lagrange** (348) 2 ♀.

59a. *Gomphus notatus* Rambur. **Jefferson**, Walker's Beach, Ohio River, Hanover, July 7, 1930. Exuvia and adult, reared by Prof. J. Speed Rogers.

60. *Gomphus quadricolor* Walsh. **Lagrange** (348) 1 ♂ 3 ♀.

*62a. *Gomphus subapicalis* Williamson. **Vigo**, pond, Pimento, June, 1929, (Donald Endicott) 1 ♀, July 4, 1929, 4 ♂; pond, three miles south of Pimento, July 4, 1929, 4 ♂. This is probably the most interesting and surprising capture in Indiana for several years as this species has been taken previously only in southern Texas.

63. *Gomphus submedianus* Williamson. **Gibson**, Foote's Lake, July 7, 1930, 2 ♀ and July 18, 1931, 2 ♂ 1 ♀. Both females captured in 1930 were ovipositing, hovering above floating pieces of partly decayed spatter dock stems and striking the abdomen against the stem. A mating pair was taken in 1931; they were flushed from a growth of low weeds near the lake and flew to a small bush where they were captured; the other male was noted to fly out over the lake with its prey (Argia sp. ♀) and was watched until it returned to the shore where it was captured.

64. *Gomphus vastus* Walsh. **Lagrange** (348) 1 ♂ 2 ♀; **Miami** (349) 1 ♀.

65. *Gomphus ventricosus* Walsh. **Lagrange** (348) 1 ♂.

66. *Gomphus villosipes* Selys. **Lagrange** (346) 1 ♂.

66a. *Gomphus viridifrons* Hine. **Lagrange** (346) 1 ♀, (348) 1 ♂ 1 ♀.

68. *Dromogomphus spinosus* Selys. **Cass** (350) 1 ♂ 1 ♀; **Lagrange** (346) 1 ♂, (348) 6 ♂ 1 ♀, (354) 8 ♂.

69. *Dromogomphus spoliatus* Hagen. **Dubois** (3371) 2 ♂.

70. *Boyeria vinosa* Say. **Morgan** (10), June 22, 1931; **Tippecanoe**, woods, five miles east of Lafayette, Sept. 5, 1932.

72. *Anax junius* Drury. **Delaware** (Ely); **Porter**, Dunes Beach, June 25, 1932 (Ely).

74. *Aeshna clepsydra* Say. **Steuben**, Lake James, Aug. 17, 1915, 1 ♂ 1 ♀.

76. *Aeshna mutata* Hagen. **Wells** (352) 1 ♂.

78. *Aeshna umbrosa* Walker. **Boone**, Zionsville, 1931; **Lawrence**, quarry pool, Moses Fell Annex Farm, July 24, 1931.

80. *Nasiaeschna pentacantha* Rambur. **Lagrange** (348) 1 ♂.

84. *Macromia pacifica* Hagen. **Boone,** Zionsville, 1931.

89. *Tetragoneuria cynosura* Say. **Kosciusko,** Webster Lake, May 29, 1932, 1 ♂ (Gould).

93. *Somatochlora ensigera* Martin. **Wells** (356) 2 ♂, (359) 1 ♂, (363) 17 ♂ 6 ♀, (357) 1 ♀.

94. *Somatochlora linearis* Hagen. **Huntington** (357) 7 ♂; **Wells** (356) 3 ♀, (359) 1 ♂, (363) 28 ♂ 2 ♀, (364) 1 ♂, (367) 1 ♂ 1 ♀, (368) 1 ♀; **Clark,** State Forest, Henryville, 4 ♂ 3 ♀, July 11-28, 1932 (P. U.), (3316) 1 ♀.

96. *Libellula cyanea* Fabricius. **Clark,** State Forest, Henryville, July 4, 1932 (P. U.); **Tippecanoe,** swamp, Lafayette, May 21, 1933 (P. U.).

99. *Libellula luctuosa* Burmeister. **Dubois** (3371); **Greene** (3365); **Marion,** Indianapolis, June 25 and July 21, 1930 (Ragains); **Morgan** (10), June 15, 1931; **Tippecanoe,** Lafayette, June 12, 1933 (Musgrave); **Warrick** (3368).

100. *Libellula pulchella* Drury. **Morgan** (10), June 15 and 20, 1931; **Spencer** (3370); **St. Joseph,** Mishawaka, June 25, July 8 and 11, 1932 (Trippel) (1); **Warrick** (3368).

101. *Libellula quadrimaculata* Linnaeus. **St. Joseph** (1).

104. *Plathemis lydia* Drury. **Boone,** Zionsville, 1931; **Delaware** (Ely); **Dubois** (3371); **Morgan** (10), June 15, 1931; **White** (3220).

105. *Perithemis tenera* Say. **Clay** (3364); **Dubois** (3371); **Greene** (3365); **Spencer** (3370); **Warrick** (3368); **White** (3220).

106. *Nannothemis bella* Uhler. **St. Joseph** (1).

107. *Erythemis simplicicollis* Say. **Boone,** Zionsville, 1931; **Delaware** (Ely); **Dubois** (3371); **Tippecanoe,** swamp, Lafayette, May 27, 1933 (P. U.); **Warrick** (3368); **White** (3220).

108. *Sympetrum ambiguum* Rambur. **Clay** (3363) 1 ♀; **Gibson** (3366) 1 ♂; **Warrick** (3368, 3369) 3 ♂.

112. *Sympetrum rubicundulum* Say. **Marion,** Indianapolis, June 25, July 28, 1930 (Ragains).

114. *Sympetrum vicinum* Hagen. **Warren** (3374).

115. *Pachydiplax longipennis* Burmeister. **Warrick** (3368).

117. *Leucorrhinia intacta* Hagen. **Tippecanoe,** Lafayette, May 13-29, 1933, 15 ♂, 2 ♀, almost all indicated from swamp (P. U.).

118. *Celithemis elisa* Hagen. **Clark,** State Forest, Henryville, July 4, 1932 (P. U.); **Warrick** (3368, 3369).

119. *Celithemis eponina* Drury. **Warrick** (3368).

121. *Pantala flavescens* Fabricius. **Morgan** (10), June 15 and July 8, 1931.

123. *Tramea carolina* Linnaeus. **Tippecanoe,** Lafayette, May 17-27, 1933, 7 ♂ (P. U.); **Washington,** carried into car as I was driving along road near Livonia, June 12, 1933.

124. *Tramea lacerata* Hagen. **Marion,** Indianapolis, June 25 and July 28, 1930 (Ragains); **Warrick** (3368).

125. *Tramea onusta* Hagen. **Huntington,** pond near Salamonie west of New Lancaster, June 30, 1929; **Morgan** (10), July 8, 1931.

MACROBRACHIUM OHIONIS, THE LARGE FRESH-WATER SHRIMP

R. N. McCORMICK, Ball State Teachers College

Macrobrachium ohionis (Smith) is a relatively little-known fresh-water shrimp locally of economic importance. Sidney I. Smith (1874) described it under the name of *Palaemon ohionis*. He states that: "The only specimens which I have seen were obtained by Professor F. H. Bradley from the Ohio River at Cannelton, Indiana, where he tells me it is taken for food." Only diagnostic external features were mentioned. S. A. Forbes (1876) found it only in the Mississippi River. W. P. Hay (1891) reported it as being captured in large numbers from the Ohio River near Lawrenceburg. Waldo L. Schmitt (1926), after a study of the more abundant tropical *Palaemonidae*, has placed this species in the genus *Macrobrachium*.

W. L. Schmitt (1933) lists the accessions to the United States National Museum as mostly from the region of New Orleans. A single record was from the State of Mississippi, a few from near the city of Savannah, Georgia, and one from North Carolina. This last mentioned one, taken in 1878, measures 102 mm. from tip of sternum to the extremity of telson. Schmitt raises the question, "Is *M. ohionis* confined to the Mississippi below St. Louis and the lower Ohio to the exclusion of the other large tributaries of these rivers?" J. N. Gowanlick of the Louisiana Conservation Commission in littora, August 17, 1931, informed me that *Macrobrachium ohionis* is a staple market article here and has an extreme delicacy of flavor. No published figure of this native species is extant.

Specimens were obtained over a period of three years (1930-32) from the Mississippi River near Chester, Illinois, and from New Orleans, Louisiana. Beside the study of preserved material observations were made on a group at the John G. Shedd Aquarium, Chicago. Others at Chester were examined alive under a binocular microscope.

This species, the "river shrimp," is distinguished from the *Penaeus* group of marine species by having only the first two pereiopods or thoracic legs, chelate, instead of three. The second one is the larger, figure 2.

Plate 1 is a photograph, approximately natural size,[1] of the two species of fresh-water shrimps. Figures 1 and 2 show ovigerous adults

[1] Reduced 20 per cent in making the cut.—Ed.

Plate 1. Fresh-Water Shrimps. Figure Titles

1. Lateral view of ovigerous *Macrobrachium ohionis*.
2. Ventral view of ovigerous adult *M. ohionis*.

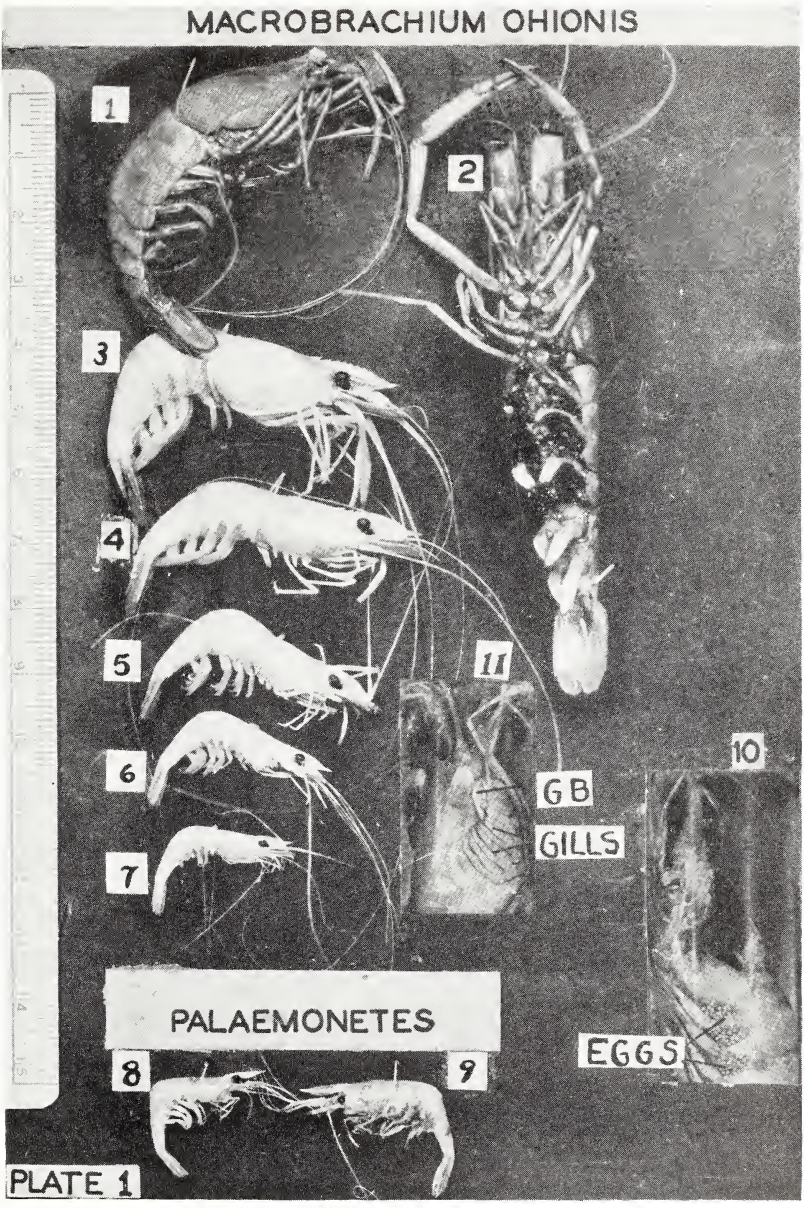
3 to 7. Different sizes (and ages) *M. ohionis*.

8, 9. Lateral view of ovigerous adults of *Palaemonetes exilipes* for comparison with *M. ohionis*.

(Above figures approximately X1. See mm. ruler)

10, 11. Lateral views of *M. ohionis*, dissected. GB, gill-bailer.

(Figures 10 and 11 slightly more enlarged than 1-9)


MACROBRACHIUM OHIONIS
1
2
3
4
5
6
7
11
GB
GILLS
10
PALAEMONETES
8
9
EGGS
PLATE 1

of *Macrobrachium*. Figures 8 and 9 are of similar egg-bearing *Palaemonetes*. Figures 3 and 7 show *M. ohionis* of various ages, while 10 and 11 are dissected *Macrobrachium*. In a representative group the ovigerous *Macrobrachium ohionis* averaged almost 80 mm. and the similarly egg-bearing *Palaemonetes* averaged 38 mm. in length. The definite flexure in the middle of the abdomen of the smaller species, figures 8 and 9, is not present in *Macrobrachium*. My observation is in accord with Forbes (1876) that *P. exilipes* has a "nearly straight rostrum with seven or eight teeth above and one or two below." The range for *Macrobrachium*, as determined from the material here studied, is from 9 to 12 dorsal rostral teeth and from one to three ventral teeth. This variation is not in favor of either sex. No marked difference in dental formula or in size appears between the upper and lower Mississippi River specimens.

The outer surface of the carapace is relatively smooth and clear. Instead of the two lateral spines being "of nearly equal size," as described by Smith (1874), the antennal spine is one-half larger than the outer and lower hepatic spine. The scattered body chromatophores and deeply pigmented eyes are striking in appearance.

The triflagellate first antenna is attached ventral to the eye. The larger flagellum of each side pointing ahead of the animal and the two flagellae arched backward over the abdomen are characteristic of the living animal and evidently are used as "feelers." The tuft of setae in the depression on the dorsal surface of the proximal joint of the peduncle marks the opening of the statocyst. Apparent exploratory movements are also made by the larger singly flagellated second antenna. On the ventral surface of the coxa is the opening of the "green gland." Injured antennae are not reflexly shed.

The mouth is bounded anteriorly by the fleshy labrum, figure 12, plate 2, and posteriorly by the two thin paragnotha, neither of which is a true appendage. Right and left are the heavy tridentrate cutting edges of the mandibles. Within the mouth and slightly dorsal to these on each mandible is a broader, tuberculated crushing and molar surface. The mandibles are connected to each other by a short heavy transverse tendon and are operated by a complex set of muscles. A three-jointed palp on each mandible is a characteristic not found in *Palaemonetes*. In order, following the mandible, are the two pairs of maxillae and three of maxillipeds. There are on the maxillae and maxillipeds integumentary configurations here designated "combs" and "brushes," figures 13 and 15.

Plate 2. *Macrobrachium ohionis*. Figure Titles

12. Mouth, lips and mandible, ventral view. (Enlarged twice as much as figures 13-18.)
13. Right first maxilla, ventral view.
14. Second right maxilla, ventral view.
15. Second maxilliped, ventral view. First gill.
16. Second thoracic leg, pereiopod, ventral view.
17. Fifth pereiopod, partly regenerated.
18. Fifth pleopod, ventral view. Typical abdominal appendage.

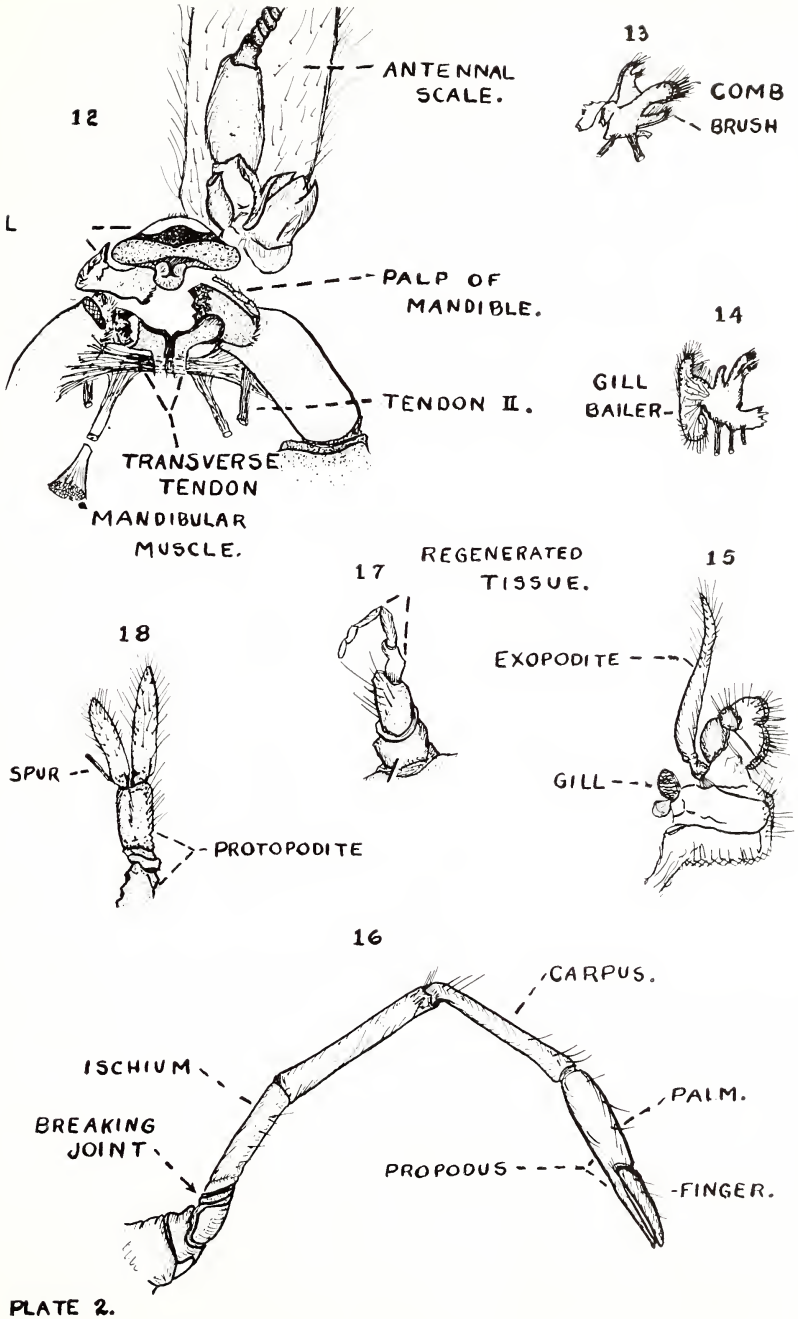

12
ANTENNAL SCALE.
L
PALP OF MANDIBLE.
TENDON II.
TRANSVERSE TENDON
MANDIBULAR MUSCLE.
13
COMB
BRUSH
14
GILL BAILER
REGENERATED TISSUE.
17
15
EXOPODITE
GILL
18
SPUR
PROTOPODITE
16
CARPUS.
ISCHIUM
BREAKING JOINT
PALM.
PROPODUS
FINGER.

PLATE 2.

Following the maxillipeds, in serial order, are five pairs of periopods or legs on the thorax. The chelate legs 1 and 2 differ from the others in having the immoble finger on a distal outgrowth of the palm of the propodus, figures 2 and 16. The means used to determine the sex is the location of the external genital pore on each side. In the female this aperture is in a setae-covered papilla on the median surface of the coxal joint of the third pereiopod. The opening of the sperm duct is

Plate 3. Shrimp Set at Chester, Illinois

in a corresponding position on the base of the fifth pereiopod. Over the ventral aperture of each of these last is a chitinous flap or valve. All five of these legs, as well as the third maxilliped, are reflexly shed and regenerated from a definite "breaking-joint," the basi-ischial suture, figure 16. The order of frequency of this appears to be: the second pereiopod (cheliped), most frequent; any one or more of the other four pairs of pereiopods; and least frequently the maxillipeds. New tissue arises from the small blood vessel canal in the middle of the diaphragm left on the basos. Figure 17 shows a later stage of growth and spe-

cialization. These observations supplement those of Florence and H. E. Wood (1932), who restudied autotomy and related phenomena in other Decopoda.

The swimmerets are alike in the two sexes. The first abdominal appendage has a reduced endopodite. A small fleshy median spur occurs on each swimmeret, figure 18, except the first and the last or uropod. The effective area of each blade is increased by a fringe of setae on each ramus. Live individuals characteristically keep up a rhythmical motion of all of these paddle-like appendages. In ovigerous females this also serves to aerate the eggs. A quick backward progression is possible as well as forward swimming, crawling or climbing.

The gill-bailer (scaphognathite) is a part of the second maxilla, figures 11 and 14. It is supported within itself by chitinous thickenings and bordered by closely set setae. Ventral to this, under the gill-cover on each side of a shrimp, is the set of seven plate-gills. They increase in size posteriorly. Gills numbers 1 and 2 are attached to the coxa of the second and third maxilliped respectively (podobranchiae). The third gill is partly attached to the anterior and dorsal part of the leg where it joins the body wall. Gill number 4 is attached somewhat higher (arthrobranchiae). The remainder are attached dorsal to the leg bases (pleurobranchiae). They appear to be very similar in pattern and position to Perrier's (1925) representation of *Palaemon*.

There is a variation in the size of the ovigerous females. There often is a considerable difference in the degree of development of the eggs and embryos from adult females captured at the same time. In a lot of 100 females examined the smallest (60 mm.) bore embryos having deeply pigmented eyes and the largest (96 mm.) had no evidence of external eggs. Eight thousand eggs were counted on the swimmerets of a representative female 84 mm. long. Specimens "in berry" have been found by the writer to have at the same time an apparently full complement of immature eggs in the ovary. As an example of the variation in size and age of those caught at a given time those taken at Chester, Illinois, on September 3 and 4, 1931, measured from 34 mm. to 90 mm. in length.

These Crustaceans are hardy and voracious. They eat both plant and animal material. "Shrimp sets" are made use of by the Chester, Illinois, fishermen. These consist of rows of green willows or cottonwood branches which are set out in shallow water and broken over so as to be partly submerged. Later, dipnets are used to catch the animals clinging to and chewing the green leaves.

In habitat and structure *Macrobrachium ohionis* is distinct from any other North American Crustacean. This report has placed on record representative morphological features and may suggest additional studies of this large fresh-water shrimp.

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THE EFFECT OF ULTRAVIOLET IRRADIATION UPON FECUNDITY OF DROSOPHILA MELANOGASTER

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The effect of ultraviolet rays upon Drosophila was studied as early as 1914 by Guyénot, whose work showed, first, that eggs subjected to ultraviolet irradiation failed to develop; second, that larvae were not affected by exposures of 15 minutes' duration, but were by exposures of 30 to 45 minutes' duration; third, that adult females irradiated after copulation laid eggs during the first three days which developed normally, but after the third day the number of non-developing eggs increased until the fifth day, after which non-development was the rule. He noted that most irradiated individuals died within fifteen days after treatment. However, he centered his attention on certain melanic forms which appeared in his irradiated strains, which he believed arose as a result of the ultraviolet irradiations. That this was true, however, he did not conclusively demonstrate.

Guyénot's work was deficient in these respects. He failed to report the age of the flies at the time of irradiation, the distance of the flies from the source of irradiation, or the temperature to which the flies were subjected at the time of irradiation. All or any of these factors would have influenced the results obtained.

Although much experimental work has been done testing the effect of ultraviolet rays on various types of animals, little has been reported in recent years relative to the effect of ultraviolet rays on Drosophila. To see if ultraviolet rays would have any pronounced effect on Drosophila the following experiments were performed.

In this set of experiments fecundity and length of life were the only factors upon which data were obtained. By fecundity is meant the total egg production of a female.

Method. Flies of the species *Drosophila melanogaster*, stock Wild D were used. The origin of this stock is unknown, but it has been kept for some years in the Purdue laboratories. Flies 12 hours or less in age were secured from the stock bottles and etherized. Males were separated from the females. After a period of 10 to 12 hours allowed to permit the flies to recover from the anesthesia, they were placed in a small wire cage about 30 mm. in diameter and 25 mm. deep. This was covered by a quartz plate 2 mm. in thickness. The flies were then exposed for various periods of time to the rays of an air-cooled quartz mercury vapor lamp (Hanovia Alpine Sun Lamp). The distance of the flies from the source of light was approximately 9 inches. The temperature at the time of exposure varied between 27° and 31° C.

For controls flies from the same stock and usually the same bottle were used. They were subjected to the same treatment as the experimental flies except that the wire cage was covered with a glass plate instead of a quartz plate. Controls were usually irradiated at the same time and under the same light and temperature conditions that the experimental flies were subjected to.

After irradiation the flies were separated into pairs, one male and one female, and each pair was placed in a shell vial 75 mm. by 22 mm. In some cases the males were not irradiated. Food consisted of a molasses-cornmeal-banana-agar mixture prepared according to Rifenburgh's formula, to which was added a drop of yeast solution. The food was heated until semi-fluid and then about one-half of a cubic centimeter was placed on a glass slide cut to fit into the vial. The semi-fluid food would flatten out on the slide providing a smooth surface. A drop of yeast solution was then added to the surface of the food. The slide was then inserted into the vial with the flies. Eggs were deposited on the surface of the food where they were easily seen. Rarely were eggs deposited on the sides of the vial.

Each day the slides were removed from the vials and the eggs counted. Usually some of the eggs had hatched before counting, in which case the number of larvae was added to the number of unhatched eggs. A new slide bearing fresh food was inserted in the place of the one removed. The flies were kept in an incubator at about 25° C.

Discussion. The experiments showed that egg laying in Drosophila was definitely inhibited by subjecting the females to ultraviolet irradiation for short periods of time. Eight or more minutes' exposure at a distance of 9 inches from the source of light resulted in almost complete sterilization. Exposure less than eight minutes in duration resulted in partial sterility. As the length of the exposure period decreased the number of eggs laid gradually increased until at 5 minutes exposure egg laying was about one-half normal.

Exposure to ultraviolet light also materially reduced the average length of life of the flies. This would obviously result in a decrease in the total number of eggs laid by the experimental flies.

Experiment	Time of exposure	No. females irradiated	No. eggs produced	Ave. No. eggs per female	Ave. life in days	Age of oldest
I	30 min.	13	0	0	5.7	7
		1	3	3	7.0	7
		1	1	1	7.0	7
II	20 min.	10	0	0	5.5	7
III	10 min.	9	0	0	4.6	7
		1	1	1	6.0	6
IV	8 min.	6	0	0	7.6	10
		16	218	13	7.2	11
		2	1,102	551	38.0	44
	control	1	1	1	note 1	.....
		8	6,069	758	note 1	.....
		7	3,100	443	note 1	.....
V	7.5 min.	3	0	0	7.3	10
		9	54	6	9.0	12
		2	480	240	16.0	19
	control	6	2,066	360	30.0	42
VI	7 min.	5	0	0	6.4	16
		25	305	13	8.3	14
		7	373	53	11.0	16
		1	121	121	8.0	8
		1	213	213	17.0	17
	control	6	4,317	719	note 2	.....
VII(a)	6 min.	7	0	0	9.1	20
		2	2	1	8.5	10
		7	226	32	12.0	31
		10	1,202	120	14.3	25
		7	3,325	475	26.6	37
	control	7	1,293	185	17.3	37
VII(b)	6 min.	11	0	0	6.2	9
		6	48	8	11.0	25
		4	161	40	10.8	14
		3	304	101	12.0	13
	control	7	2,444	349	note 3	.....
VIII	5 min.	10	2,747	274	22.0	37

Note 1—eggs were counted for only 11 days.
Note 2—eggs were counted for only 25 days.
Note 3—eggs were counted for only 12 days.

Other experiments showed that the time of irradiation was of importance. Flies exposed to ultraviolet rays within five hours after emergence were rendered sterile by short exposures. Flies more than 24 hours old were much more resistant to ultraviolet irradiations than flies

less than 24 hours old. This was probably due to the fact that the pigment which developes in the epidermis was incompletely developed for a period of a few hours after emergence. Also very young flies were much less viable and were much more liable to become caught in the food media. Or it may be that the developing ova were much more susceptible to the effects of the rays during the period immediately after emergence than later.

Males were more resistant to ultraviolet irradiations than females. Much longer periods of irradiation were necessary to bring about sterility. Irradiated males lived on an average longer than did irradiated females.

Experiment 7a showed irregularities which were not readily accounted for. Controls showed a lessened egg production and were shorter lived than the experimental flies. The fact that several of the experimental and the control flies died on the 13th day after irradiation suggests the possibility that some environmental factor might have been involved, for example a sudden rise in the temperature of the incubator.

In experiment 4, two irradiated flies showed a near-normal egg production. This might have been due to the individual resistance of these flies or it may have been that with a large number of flies in a small cage during irradiation, these two might have been partially shielded from the full effects of the ultraviolet rays.

It is the writer's belief that in nature, ultraviolet irradiations might play an important part in the reproductive activities of insects. Under some conditions, ultraviolet rays might stimulate egg production, under other conditions, inhibit it. There is a possibility that ultraviolet light because of its sterilizing power might be used in the control of certain insect pests.

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BIRDS OF TIPPECANOE COUNTY—IV

LOUIS A. TEST and FREDERICK H. TEST, West Lafayette, Indiana

This is the fourth of a series of papers dealing with the avifauna of Tippecanoe County, completing the annotated list of the birds reported from the county. The total reported to date is 230.

190. *Passer domesticus domesticus.* (Linnaeus). English Sparrow. (688.2). Butler in his "Birds of Indiana" says that the English sparrow was first introduced in Lafayette about 1874. They increased rapidly and were very abundant in Tippecanoe County when the senior writer first came to Lafayette in 1888. They were then nesting abundantly everywhere about the town. In the past few years this bird does not seem to have increased so rapidly and is only holding its own or possibly decreasing in numbers. This is particularly noticeable in the cities, perhaps due to the almost complete disappearance of the horse in the towns. The proportion of birds in the country as compared to the cities is much larger than formerly. They begin nesting early in the spring and raise several broods in a season. It will be interesting to note what effect the starling will have upon this species, as they use similar nesting sites.

191. *Dolichonyx oryzivorus.* (Linnaeus). Bobolink. (494). The bobolink 40 years ago seems to have been rather rare in Tippecanoe County and, when found, was quite locally distributed. At that time a few nested regularly on certain farms east of Lafayette and in spring were sometimes seen in a clover field forming a part of the Purdue Campus. In August, flocks were occasionally seen in the meadows near the Wabash river south of Lafayette. They seem gradually to have become more common and are now a not uncommon summer resident of the county. They are still somewhat irregular in occurrence and quite locally distributed. Alfalfa fields seem to be the favorite nesting sites. During the migrations the bobolink is more common than in the nesting season. In the spring they usually arrive around the first of May, and, probably, most of them leave in August (though late summer records are few). The earliest spring date is April 25, 1904, from the records of the Purdue Bird Club. Other dates are April 29, 1928 (M. W. Gardner), May 5, 1890, May 4, 1932, May 7, 1931; a late date for spring arrival is May 10, 1926. Fall dates are Aug. 8, 1932 (flock of 12), Aug. 17, 1893 (large flock), and an unusually late date, Sept. 28, 1929, when D. R. Burtsfield reports a flock of 30.

192. *Sturnella magna magna.* (Linnaeus). Eastern Meadowlark. (501). The meadowlark is an abundant summer resident in the county, and some few are resident in favorable localities. One was flushed a few years ago from under a snow covered tuft of alfalfa in a field just west of West Lafayette. Some years ago they were seen near town nearly every winter but the past few winters few have been seen, possibly due to lack of proper cover. The migrant birds generally arrive in February and become common early in March. Nest and eggs are found by the middle of April. In the fall most of the meadowlarks have left by early November.

193. *Agelaius phoeniceus phoeniceus.* (Linnaeus). Eastern Redwing. (498). This red-winged blackbird is an abundant summer resident, breeding commonly in all the swamps of the county. These birds are among our earliest spring migrants, arriving in large flocks, but we have no records to indicate that they ever spend the entire winter here. Breeding begins in late April or early May, and the young are mostly out of the nest by early June. It is not until late in the fall that the last flocks depart; so there are only two or three months in the year in which the red-wings are absent from the county. Early dates of arrival and late dates of departure are February 13, 1932 and November 19, 1931. Average dates would be about March 1, and November 10. As swamps are drained this bird will undoubtedly become less abundant.

194. *Icterus spurius.* (Linnaeus). Orchard Oriole. (506). This oriole was formerly much more common in the county than it is now. At present it can not be called a common bird, though some nest in the county each year, and it is a summer resident as well as migrant. The average time of arrival in the spring is about May 1. Early and late spring dates are April 24, 1904 (Purdue Bird Club), and May 17, 1928 (Max Gardner). Skins and eggs are in our collection.

195. *Icterus galbula.* (Linnaeus). Baltimore Oriole. (507). This attractive bird is a common migrant and summer resident of Tippecanoe County and is well known because of its bright colors and characteristic nest. The time of arrival in the spring is quite regular, being the last week in April or first week in May. Nesting begins soon after arrival, and the young are out of the nest about the middle of June. Early and late dates of spring arrival are April 22, 1927, and May 4, 1924. They usually are common soon after the first arrivals appear.

196. *Euphagus carolinus.* (Müller). Rusty Blackbird. (509). The rusty blackbird can hardly be called common but is not an uncommon migrant and, sometimes, winter visitor in the county. It may be more common than records would indicate as it is probably frequently confused with the bronzed grackle. Early and late spring dates are March 2, 1902 (Purdue Bird Club), and April 27, 1927 (D. R. Burtsfield). Fall dates are October 17, 1929 (D. R. Burtsfield), and November 14, 1903. Skins are in our collection.

197. *Quiscalus quiscula aeneus.* Ridgway. Bronzed Grackle (511b). The bronzed grackle is an abundant summer resident and migrant and, in less numbers, a resident in the county. There are records at Lafayette for every month in the year and some winters flocks of 75 or more winter in the towns or around chicken yards and hog pens. The bulk of the birds arrive in February and leave in November. They are usually common before March 1 and remain so until well into November. They nest rather early, and young out of the nest were noted May 24, 1929 (D. R. Burtsfield). The grackles certainly are not decreasing in numbers and, possibly, are becoming more abundant.

198. *Molothrus ater ater.* (Boddaert). Eastern Cowbird. (495). The cowbird is an abundant summer resident and migrant and, perhaps very rarely, a resident, as we have one January record (January 3, 1927). The most of them arrive early in March and leave in Novem-

ber. Early spring and late fall dates are March 8, 1932, and November 24, 1931.

199. *Piranga erythromelas.* Vieillot. Scarlet Tanager. (608). The scarlet tanager 40 years ago was a common migrant and summer resident in some numbers in the county, and flocks were frequently seen on the Purdue Campus during the spring migration. At the present time this bird can hardly be called common, though it is still a regular migrant and nests. The spring migrants usually arrive towards the last of April or early in May but records for their departure in the fall are lacking, probably due to the fact that the female and male in fall plumage are both inconspicuous. Early and late spring dates of arrival are April 25, 1896, and May 11, 1929. Skins are in our collection.

200. *Piranga rubra rubra.* (Linnaeus). Summer Tanager. (610). The only record we have for this county is a sight record by D. R. Burtsfield, who on July 10, 1929, saw one male at Ross Camp in the southern part of the county. It would seem that the range of this bird might occasionally include Tippecanoe County.

201. *Richmondena cardinalis cardinalis.* (Linnaeus). Eastern Cardinal. (593). The cardinal is a common resident of Tippecanoe County and nests commonly, both in the towns and country, wherever shrubbery and undergrowth afford cover. Banding records seem to indicate that the cardinal does not migrate but spends its life in a rather restricted area. In the winter these birds are sometimes seen in small flocks. Nests with eggs are found the latter part of April. The cardinal is extending its range northward in Indiana and is probably more common in the county than formerly.

202. *Hedymeles ludovicianus.* (Linnaeus). Rose-breasted Grosbeak. (595). The rose-breasted grosbeak is a common migrant and, more rarely, a summer resident in the county. It is found both in the towns and in the wooded districts of the country. Spring migrants usually arrive late in April. Typical dates of arrival are April 24, 1904, and 1921, April 28, 1894, May 6, 1903, 1927, 1929. A late fall date is Oct. 8, 1927. Skins and eggs are in our collection.

203. *Passerina cyanea.* (Linnaeus). Indigo Bunting. (598). A common migrant and summer resident throughout the county wherever there is undergrowth or brush for cover. In the spring they arrive about May 1 and are soon nesting. An early date is April 20, 1902 (Purdue Bird Club) and a late date May 11, 1928 and 1929. There are no fall records. A nest with four eggs was found August 8, 1932, at Headley's Lake, and the young were banded August 25. The indigo bunting does not seem to be decreasing in numbers.

204. *Spiza americana.* (Gmelin). Dickcissel. (604). The dickcissel is a common migrant and summer resident throughout the county wherever there are open meadows. It formerly nested on the Purdue University Campus. The spring migrants usually arrive early in May and are in full song when they arrive. Early and late dates of arrival are April 17, 1902 (Purdue Bird Club) and May 12, 1903 (Purdue Bird Club) and 1926. Full records are lacking. Skins and eggs are in our collection.

205. *Hesperiphona vespertina vespertina.* (Cooper). Eastern Evening Grosbeak. (514). The only record of the evening grosbeak for the county is that of a specimen, shot from a small flock, by H. N. McCoy February 1, 1890, about 1½ miles northwest of the Purdue University Campus. The skin was given to the Richmond, Indiana, High School.

206. *Carpodacus purpureus purpureus.* (Gmelin). Eastern Purple Finch. (517). The purple finch is a regular migrant in the county, at times seeming to be fairly common, at others rather rare. It usually arrives early in the spring and possibly winters here occasionally or at least is a winter visitor. Early spring dates are February 23, 1929 (D. R. Burtsfield) and March 1, 1926. A late spring date is April 29, 1902 (Purdue Bird Club). A fall date is October 18, 1929 (D. R. Burtsfield).

207. *Spinus pinus pinus.* (Wilson). Northern Pine Siskin. (533). The pine siskin seems at present to be a rather rare migrant in this county as recent records are very few. Formerly it was seen more frequently and while never common could hardly be called rare. Possibly it was then at times a winter resident. The skins of a male and female in our collection both bear the date Feb. 22, 1897. A recent late spring date is April 27, 1929 (D. R. Burtsfield).

208. *Spinus tristis tristis.* (Linnaeus). Eastern Goldfinch. (529). The goldfinch is a common migrant and summer resident, and in less numbers a resident, of the county; some always wintering here. They usually become common in April and remain in flocks until the breeding season in July. In the fall the most of them leave in September or October.

209. *Loxia curvirostra pusilla.* Gloger. Red Crossbill. (521). The crossbill seems at present to be a rare visitor to the county as there are almost no records for the past 15 years. Formerly these birds were frequently quite common in the spring and early summer, and it is barely possible they may have nested. In 1892 they were seen frequently from March 11 to June 30. In 1895 from March 30 to May 22, and in 1897 from February 22 to May 24. At that time there was an extensive windbreak of evergreens on the north side of the Purdue Campus and an abandoned evergreen nursery ¼ mile north which the birds frequented. Now the nursery is gone, and the windbreak has all but disappeared, and with them has gone the crossbill. A number of skins are in our collection.

210. *Pipilo erythrophthalmus erythrophthalmus.* (Linnaeus). Red-eyed Towhee. (587). The towhee is a migrant and common summer resident of the wooded areas of the county. There seems to be no noticeable increase or decrease in numbers except that as wooded areas get smaller fewer can find nesting sites. It is possible that it is a rare winter resident as there is one winter date, January 1, 1906. The migrants usually arrive in March and are soon common. Early and late spring dates of arrival are March 8, 1902 (Purdue Bird Club) and March 27, 1932. In the fall they usually leave in October. A late date is October 29, 1928 (D. R. Burtsfield).

211. *Passerculus sanwichensis savanna.* (Wilson). Eastern Savannah Sparrow. (542a). The savannah sparrow is a spring migrant but seems rather rare except in the prairie sections of the county. Possibly it is confused with other sparrows and may be more common than reports would indicate. It was quite common on the Wea plains April 16, 1932. Early and late spring dates are April 7, 1929, and May 3, 1925. There are no fall records.

212. *Ammodramus savannarum australis.* Maynard. Eastern Grasshopper Sparrow. (546). The grasshopper sparrow is a migrant and summer resident. Locally it may be fairly common and in other places nearly or entirely lacking. Being inconspicuous it is often overlooked. They were quite common on the Wea Plains April 16, 1932. We have no fall records.

213. *Passerherbulus henslowi henslowi.* (Audubon). Western Henslow's Sparrow. (547a). Henslow's sparrow seems to be quite rare in the county as we have but one sight record, April 7, 1929, when two were seen about a mile northwest of West Lafayette. Probably it is more common than our records indicate.

214. *Pooecetes gramineus gramineus.* (Gmelin). Eastern Vesper Sparrow. (540). The vesper sparrow is a common migrant and less common summer resident in the county. They usually arrive about April 1 and leave in October. Early and late dates of arrival are March 23, 1929 (M. W. Gardner) and April 25, 1925. A late fall date is November 9, 1902 (Purdue Bird Club). This bird does not appear to be as common as 25 years ago. Skins are in our collection.

215. *Chondestes grammacus grammacus.* (Say). Eastern Lark Sparrow. (552). Migrant and summer resident, formerly fairly common but for the past 25 years has been much less common and now appears to be rare. No reason has been assigned for this great decrease in numbers in recent years, for the localities where the bird formerly was found have not changed greatly. Some Purdue Bird Club dates are: April 24, 1902, April 23, 1903, 1904. The only recent record is May 8, 1921, when a single specimen was seen. Skins are in our collection.

216. *Aimophila aestivalis bachmani.* (Audubon). Bachman's Sparrow. (575a). Bachman's sparrow never has been common in the county, but 25 or 30 years ago was reported occasionally. It was a migrant and summer resident and nests have been found. All of our records are for May. The skins of two males in our collection bear the dates May 28, 1904 and May 15, 1906. These were both taken near Lafayette. There are no records for the past fifteen or twenty years.

217. *Junco hyemalis hyemalis.* (Linnaeus). Slate-colored Junco. (567). The slate-colored junco is an abundant migrant and common winter resident. Banding records show that some birds, at least, stay in the same locality for some months during the winter. They usually arrive near the middle of October but are occasionally earlier. Early and late fall dates of arrival are September 21, 1933 and October 19, 1928 and 1931. Another early date is September 22, 1894. The date of departure is usually late in April but sometimes extends into early May. Typical dates are April 21, 1925, April 26, 1930, May 2, 1893.

Early and late dates are April 17, 1927 and May 13, 1931. The latest banding record is May 5, 1933. The birds are often in song before they leave.

218. *Junco oreganus shufeldti.* Coale. Shufeldt's Junco. (567b). The only known record of Shufeldt's junco in Indiana was a specimen killed in West Lafayette on January 20, 1891, by R. S. Wickersham who killed the bird with a sling shot and brought it to one of the writers as food for a captive barn owl. The bird was recognized as something different from the ordinary junco, so was skinned and sent to the Smithsonian Institution for identification. The skin has recently been resubmitted and the identification confirmed by H. C. Oberholser. This skin is now in the collection of A. W. Butler at Indianapolis.

219. *Junco oreganus montanus.* Ridgway. Montana Junco. (567f). A junco which the writers caught in their yard in West Lafayette and banded was identified by them as this species. The bird was captured and banded November 29, 1928 and repeated in the same trap January 3, 1929. The identification was made with the aid of various standard keys, especially Chapman's and by comparison with skins of several species of juncos in our collection, and the writers feel they are quite sure of the identification.

220. *Spizella arborea arborea.* (Wilson). Eastern Tree Sparrow. (559). The tree sparrow is a regular and common migrant and probably winter resident of the county. They usually arrive about the middle of October, are common through the late fall and winter and leave in March and early April for their breeding grounds in the north. An early date of arrival is October 14, 1928 (D. R. Burtsfield), and the latest date of departure in the spring is April 19, 1904 (Purdue Bird Club). Skins are in our collection.

221. *Spizella passerina passerina.* (Bechstein). Eastern Chipping Sparrow. (560). The chipping sparrow is a migrant and common summer resident throughout the county nesting commonly on the Purdue Campus and in the yards of Lafayette and West Lafayette. They are usually singing at the time of arrival and are mated soon after. They usually arrive about the middle of March and leave about the middle of October. The earliest dates of arrival are March 19, 1894, and 1903, and an exceptionally late date is April 12, 1932. The latest fall date is October 27, 1902 (Purdue Bird Club).

222. *Spizella pusilla pusilla.* (Wilson). Eastern Field Sparrow. (563). An abundant migrant and summer resident, nesting wherever there are open woods and fields neighboring open woods. They are quite regular in their arrival in the spring, appearing soon after the middle of March, and are usually singing when they arrive. Our earliest spring date is March 13, 1927 and a late date April 3, 1921. An average date is March 24, 1904 and 1928. Early and late fall dates of departure are October 2, 1929 (D. R. Burtsfield) and October 25, 1924.

223. *Zonotrichia querula.* (Nuttall). Harris's Sparrow. (553). Harris's sparrow evidently is a rare migrant for we have but two records, both in 1933. Tippecanoe County would seem to be at the extreme eastern edge of the range of this bird, though some are found regularly in the Chicago district. May 6, 1933, D. R. Burtsfield brought

to us for identification an adult specimen, which he had just caught and banded at his station in West Lafayette. The bird was released in our yard and May 9 was caught in one of our traps a quarter of a mile from our yard. September 27, 1933, Burtsfield brought to us an immature Harris's sparrow which he had caught at the same place as the first one. Evidently this species is extending its range as there are no previous records for the county.

224. *Zonotrichia leucophrys leucophrys.* (Forster). White-crowned Sparrow. (554). The white-crowned sparrow is a fairly common migrant, apparently more common in the spring than the fall. In the spring they usually arrive around May 1 and leave towards the last of the month. The earliest recorded date of arrival is April 19, 1904 (Purdue Bird Club) and the latest date of departure May 23, 1931. Fall records are few but there are two for 1928, September 29 and October 19. Both are by D. R. Burtsfield. This species seems to be about as common as formerly. There are skins in our collection.

225. *Zonotrichia albicollis* (Gmelin). White-throated Sparrow. (558). The white-throated sparrow is an abundant migrant about equally common in spring and fall. In the spring they usually arrive in April but are somewhat irregular in the date of arrival. An extremely early date is March 4, 1894. A late date of arrival is April 24, 1925 and 1926. A late date of departure is May 22, 1904 (Purdue Bird Club). In the fall they arrive in late September or early October and leave in late October or early November. Early dates of fall arrival and late date of departure are September 20, 1929 and November 5, 1931. There are skins in our collection.

226. *Passerella iliaca iliaca.* (Merrem). Eastern Fox Sparrow. (585). The fox sparrow is a common migrant both in spring and fall. It may rarely be a winter visitor or resident as we have one winter date, January 2, 1925, when one was seen on the Purdue University Campus. It usually arrives in March, an early date being March 4, 1904 (Purdue Bird Club), and leaves in April; a late date is April 19, 1904 (Purdue Bird Club). In the fall the first arrivals come in late September or early October and leave in late October or early November. Early and late fall dates are September 27, 1928 (D. R. Burtsfield) and November 15, 1931. Skins are in our collection.

227. *Melospiza lincolni lincolni.* (Audubon). Lincoln's Sparrow. (583). The Lincoln sparrow is a regular migrant in both spring and fall. It is rarely reported but banding records indicate that it is not uncommon and is overlooked rather than absent. In the spring they are present during May. Early and late dates are May 2, 1925 and May 21, 1931. Fall dates are few. An early one is September 19, 1931 and a late one October 17, 1933 (D. R. Burtsfield).

228. *Melospiza georgiana.* (Latham). Swamp Sparrow. (584). The swamp sparrow is not an uncommon bird in the county but is undoubtedly confused with the song sparrow and is seldom reported. All our records are for the spring and range from March 6, 1894 to May 3, 1932. There are skins in our collection and several banding records. There is no record of this sparrow breeding in the county.

229. *Melospiza melodia beata.* (Bangs). Mississippi Song Sparrow. (581u). The song sparrow is an abundant resident in Tippecanoe County, many staying in the same locality through the year. They begin to sing in February and are nesting by early April. Two or three broods are reared each season. There is no noticeable decrease in this species in the past 40 years.

230. *Calcarius pictus.* (Swainson). Smith's Longspur. (537). The only record for this longspur is April 16, 1932, when eight were seen on the Wea Plains five miles south of Lafayette. A female was secured and the skin is in our collection. This species may be more common than this single record indicates.

THE GROSS ANATOMY OF A TWO-BODIED LAMB

T. W. TORREY, Indiana University

Through the courtesy of a student, Mr. J. L. Fuelling, there came to my hands late last spring a female lamb exhibiting an interesting duplication of limbs and hind parts of the body. Such monstrosities are, of course, not uncommon, yet because each is usually a little different than any of the others, it seems worth while to make a record of the more gross abnormalities.

The animal in question is reported to have lived for about two hours, having been delivered by a veterinarian from a sheep which had borne a normal lamb the day before. At death it was embalmed with a phenol mixture and thus reached me in a fair state of preservation. I immediately turned the specimen over to two interested students, Mr. Maxwell Power and Mr. W. C. Davis, who carried out the dissections under my direction. Subsequently I made certain supplementary dissections myself.

Externally the lamb presented a single normal-sized head and neck and an undivided though excessively large trunk as far as the middle of the abdomen. At this level there was an abrupt bifurcation of the body, the two portions being complete, full-sized, and each possessed of a tail and pair of hind-legs. The fore-legs were likewise duplicated, but one pair occupied a useless position on the dorsal side of the body. The second pair would have served very creditably.

Observations on the internal anatomy were made from the ventral side, beginning first in the laryngeal region and carried progressively backward.

In the neck a perfectly regular arrangement of organs prevailed. Larynx, thyroid, blood-vessels, etc. appeared to be normal.

Modification of the thoracic cavity and its contained organs consisted primarily of increase in size. The volume of the cavity itself was at least a third above average, being correlated with the peculiar skeletal arrangement of this region to be described below. The lungs were

in a collapsed state but exhibited the size and distinct lobulation characteristic of the sheep. They enveloped in regular fashion the centrally located pericardial cavity and heart. This latter organ was considerably enlarged, but otherwise unchanged.

The first conspicuous departure from normal was seen in the derivation of blood vessels, particularly the arterial trunks, from the heart. The single aorta coming from the left ventricle assumed a T-shape configuration and sent large posterior aortae to the right and to the left. These proceeded along the dorso-lateral walls of the thorax, giving off branches en route, gradually diverging as they passed through the abdominal cavity until they came to be isolated in the separate bodies. The tributary vessels were not worked out. From the arching top of the T arose three arterial trunks, one median and two lateral. The former, identified as the common carotid, immediately divided into two anteriorly proceeding external carotids. The lateral vessels were right and left subclavian respectively.

This represents a considerable departure from the usual situation consisting of a single aortic arch from which is derived, on the one hand, a brachio-cephalic giving rise to carotids and right subclavian, and on the other, a left subclavian.

The anterior vena cava showed no distortion. Two separate postcavas, however, ran from each division of the body and united just posterior to the diaphragm. The single vessel thus formed almost immediately received the hepatic vein and continued on to the heart in normal fashion.

Even more extensive structural duplication was seen in the abdominal cavity. Single in its beginnings, this cavity bifurcated and extended into each of the two complete bodies. There was, however, no dividing septum; the cavity was a single one, having merely a Y-shaped contour.

The esophagus pierced the dorsal side of the diaphragm and entered the single typical ruminant stomach. Leaving the stomach was the small intestine which for the first five and one-half feet of its length continued as a single tube. At this point it forked and each portion proceeded into its respective half of the body cavity. Two feet from the point of division on each side were found fully developed caeca, which marked the beginnings of the two large intestines. Both of these were about two and one-half feet in length and each finally terminated in an anus.

The organs associated (anatomically) with the digestive tube, i.e., liver, pancreas, spleen, showed no duplication. As far as could be determined their relations to the neighboring organs were regular.

Duplication in the excretory system was also apparent. Without going into the details of their connections, it may be said that there were two bladders, each receiving a pair of ureters from a corresponding pair of kidneys. These latter consisted of a large dorso-lateral pair and a dorso-median pair of about half size. Anterior-dorsally located adrenal bodies were associated with each kidney, those of the middle being proportionally reduced in size.

The immaturity of the reproductive organs made their dissection impracticable.

The most profund modifications were those involving the extensive duplication of skeletal parts. Whereas the abdominal cavity and its organs were only partly duplicated and the thoracic cavity not at all, almost two complete axial skeletons were present.

The cranium, of course, was single, but the first cervical vertebra, the atlas, consisted of two verterbrae with their median transverse processes fused. The two sets of articular processes thus present articulated with correspondingly enlarged occipital condyles at the base of the skull. Two complete vertebral columns proceeded posteriorly from this single fused atlas. The remaining six pairs of cervical vertebrae lay closely parallel to each other, loosely bound together by ligaments. At the level of the first thoracic vertebra the two columns diverged abruptly and extended posteriorly into the separate bodies until they terminated in the tail.

Each axis had a complete set of ribs. Those in the lateral positions were normal in size; those between the two columns, considerably shortened and the first three pairs unattached at their distal ends. The ribs of the right side of the right column and left side of the left united ventrally with a normal sternum. The shortened median ribs curved upwards and, with the exception of the aforementioned first three, attached to an improvised dorsal sternum.

Two pairs of normal scapulae were present with their associated fore-legs. The median member of each pair of legs lay on the dorsal surface of the thorax; the functional limbs represented the lateral members of the two pairs.

The two widely separated sacra with their pelvic girdles and appendages were in no way distorted.

The nervous system exhibited a duplication of parts to correspond to the double vertebral column. At the level of its emergence from the cranium through the foramen magnum, the spinal cord bifurcated and passed as two cords through the two neural canals of the fused atlases into the individual columns.

No observations were made on the distribution of muscles.

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[1] Addresses given are the latest on file. If address is known to be incorrect, the address is followed by (I).

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[2] Figures following M, F, and NR indicate date of election to membership, fellowship and non-resident fellowship respectively.

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Beghtel, Floyd E., Evansville College, Evansville M25
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Betzner, Ruth A., Bunker Hill M26
Bird, Sylvia L., R. R. No. 1, Mooreland M31

Bisch, Bernard J., St. Mary-of-the-Woods.....M33
Bishop, George, Mitchell.....M27
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Bjorklund, J. Harman, North Manchester.....M32
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Blaydes, Glenn William, 213 West Weber Road, Columbus, Ohio..M23
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Boggs, Alton H., R. F. D. 6, Warsaw.....M30
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Bolen, Homer R., Cape Giradeau, Missouri.....M22
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Boring, Mrs. Opal H., Milroy.....M28
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Brock, James E., R. R. No. 1, Marion.....M22
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Brown, H. Paul, Kurtz.....M30
Brown, Louis F., Windfall.....M28
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Brubaker, Ralph, 1150 Portage, South Bend.....M32
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Bryant, Dora, Clarkshill....M31
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Bufler, Dorothea E., 112 East Sycamore Street, Liberty....M30
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Burkhart, Peter A., Marr, Ohio....M29
Burnett, Arthur, Bloomington....M27
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Caufman, Grace, Gallipolis....M30
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Childs, Lewis, West Baden.....M26
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Clowes, G. H. A., c/o Eli Lilly Company, Indianapolis.....M20
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Coffel, Hal Herbert, Pennville.....M23
Coffing, Charlene, 3332 Graceland Avenue, Indianapolis.....M33
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Collins, George, University of Notre Dame, Notre Dame.....M33
Conaway, Martin Wesley, 1430 Terrace Avenue, Indianapolis....M33
Condon, W. Chalmer, R. R. No. 2, Logansport.....M28
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Conner, S. D., 204 South Ninth Street, Lafayette.....M12
Conover, James F., 2230 North 7th Street, Terre Haute.....M25
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Corley, Ralph Conner, Dept. Chemistry, Purdue University, Lafayette M32
Corns, Marjorie, R. R. No. 3, Vevay.....M30
Cortez, Samuel H., State College, Mississippi.....M32
Coryell, H. N., Dept. Geology, Columbia Univ., New York City, New York M14
*Coulter, Stanley, c/o Eli Lilly & Co., Indianapolis (Honorary Fellow 1928) .....M Charter, F93
Cover, H. S., Chippewa Knoll, South Bend.....M30
*Cowles, Henry C., Dept. of Botany, Univ. of Chicago, Chicago, Illinois M26, F30
Cox, Alvalon, 2948 Indianapolis Ave., Indianapolis.....M28
Cox, C. F., 528 North Oxford Street, Indianapolis.....M22
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Cravens, Irene E., Bloomfield....M30
Craw, Joe R., Hagerstown....M29
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Crouch, Frances E., Hanover....M27
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Davis, Marvin R., R. R. No. 5, Greensburg....M29
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De Vol, Charles E., Luho, Ku, China....M28
DeVries, Thomas, 521 Vine Street, West Lafayette....M26
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Dietrich, Irene, Borden....M30
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Dolan, Joseph P., Syracuse....M95
Dolby, George Paul, R. R. No. 7, Box 36, Huntington....M31

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Evans, Frank C., Crawfordsville.....M29
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Finster, Ethel B., Mathiston, Mississippi (I).....M23
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Fleetwood, Charles W., Kurtz.....M30
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Fletcher, Worth A., Dept. Chem., Univ. Wichita, Wichita, Kansas..M26
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Frushour, J. H., Oldenburg....M30
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Garner, Murvel R., Earlham College, Richmond....M25
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Gassensmith, Rev. Frederick M., University of Notre Dame, Notre Dame M27
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Geisler, Walter C., 2267 North Dearborn St., Indianapolis....M30
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Gettelfinger, Wilfrid C., Ramsey....M28
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Gingery, Walter G., Washington High School, Indianapolis....M18

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Glenn, Gail Geneve, Ramsey.....M28
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Goldsberry, W. N., Greencastle.....M31
Goldsmith, William M., Dept. Embryology, Univ. Wichita, Wichita, Kansas.....M14
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Graham, Frank V., Ball Teachers College, Muncie.....M20
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Guthrie, Ned, Hanover College, Hanover.....M27
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Hazlett, Donald C., Russellville..... M30
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Heaton, Robert R., Rushville..... M32
Hebert, Peter E., Notre Dame University, Notre Dame..... M27
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Higgins, Frank R., 1719 North 9th Street, Terre Haute..... M25
Higgins, Kenneth E., 207 South Arlington Ave., Indianapolis..... M31

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Hunter, Mrs. Stephen, Ridgeville M25
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Hutchinson, Emory, Norman Station M15
Hutton, Joseph G., State College, Brookings, South Dakota M11
Hyatt, George F., R. R. No. 2, Versailles M25
Hyatt, Joseph Lewis, Hanover College, Hanover M30
Hyman, Hugh H., Galveston M30
Imel, Mary Marjorie, Fairland M31
Inskeep, Anna M., Monticello M24
Irons, Vernal, Jasonville ..... M

Irving, Thomas P., University of Notre Dame, Notre Dame.....M14
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Jefferson, Louise P., Springport.....M26
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Johnson, Lela L., New Harmony.....M31
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Johnson, Willis H., Wabash College, Crawfordsville.....M28
Johnston, Robert M., University of Notre Dame, Notre Dame.....M32
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Kemper, Mary Esther, Morristown.....M31
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Kimmell, Anna May, Kimmell.....M30
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Kinnet, Russell, Milroy.....M23
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Kintner, Kenneth E., 1004 East Street, North Manchester.....M29
Kintner, M. Quentin, 1004 East Street, North Manchester.....M33
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Lee, George H., Westfield....M32
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Lefler, Glenn Q., Warren....M28
Lehman, Rachel M., Box 50, Westervelt, Illinois....M28
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Lemon, Lola May, Larwill....M29
LeRoy, Ernest E., 39 Lake Avenue, Williamson, New York....M30
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Liston, Jesse G., R. R. No. 2, Lewis....M16
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Loughridge, Gasper Arthur, Goodland....M23
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Lyons, Robert E., 630 East Third Street, Bloomington.....M31
McAllister, Rev. Charles, St. Thomas Military Academy, St. Paul, Minnesota M28
McAtee, W. L., 200 Cedar Street, Cherrydale, Virginia.....M28
McAvoy, Blanche, Illinois State Normal Univ., Normal, Illinois....M21
McClelland, Earl F., 59 West Banta Street, Franklin.....M30
McClintock, Ralph B., Park House, Sunnyside Park, L. I., New York M26
McConaha, Fred, Oakland....M30
McConaha, Marjorie, Centerville....M32
McCormick, Robert N., 508 South Talley Ave., Muncie.....M31
McCoy, Ralph W., Williams....M33
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McDonald, Clinton C., Univ. of Wichita, Wichita, Kansas.....M22
McEachron, Karl B., 23 Waverley Street, Pittsfield, Massachusetts..M21
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McKee, Madge, Goodland....M29
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McKeon, Rev. Frederick T., University of Notre Dame, Notre Dame M27
McMillan, Frances, St. Mary's College, Notre Dame.....M32
McMillan, Ona, Franklin....M30
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Martin, Frank D., 215 Waldron Street, Lafayette.....M26
Martin, Lois E., Walton.....M30
Martin, R. Earl, Hanover.....M25
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Martin, Walter E., 453 Littleton Street, West Lafayette.....M33
Martindale, Ruth, Clermont.....M30
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Matthews, Mary L., 629 Waldron Street, West Lafayette.....M24
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Michael, Curtis B., Cross Plains.....M26
Michael, Lyle Jordan, Indiana Central College, Indianapolis.....M22
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Middleton, Robert E., Essex, Ontario, Canada.....M24
Mikesell, Herbert Sumpter, Richmond Ave., Richmond.....M30
Miles, Everett E., 4126 Arlington Ave., Fort Wayne.....M31
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Miner, Wallace B., Indiana Central College, Indianapolis.....M28
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Mitchell, Elta Alden, R. R. No. 3, Franklin.....M33

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Mozingo, Ralph V., Franklin M31
Mullen, Lowell, Lakeside, Washington M25
Mullendore, Neomi, Franklin M22
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O'Neal, Claude E., Ohio Wesleyan University, Delaware, Ohio.....M12
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Owen, Mrs. Marjorie B., 2202 Portage Ave., South Bend.....M28
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Painter, Henry R., Box 495, Lafayette.....M21
*Palmer, C. M., Butler University, Indianapolis.....M25, F29
Parfitt, Elliott H., 1025 Third Street, West Lafayette.....M23
Parker, Dorothy, Bargersville.....M31
Parker, Druley, Shortridge High School, Indianapolis.....M30
Parker, William A., Indiana University, Bloomington.....M31
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Pearce, Joseph Roberts, Willow Hill, Illinois.....M24
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Pedlow, J. Thomas, 511 East Anderson Street, Greencastle.....M28
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Pence, Samuel Raper Jr., Rossville.....M30
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Pittman, Lenard E., Fairbanks M26
Plasterer, Eiffel G., 213 Wright, Huntington M29
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Rankin, Horace, c/o Shell Petroleum Corp., Tyler, Texas (I) M27
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†Ransom, James H., James Millikin Univ., Decatur, Illinois .. F02, NR18

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Rechenberg, Elizabeth Anna, 805 Brown Street, Valparaiso.....M27
Records, Ralph L., Edinburg.....M20
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Reed, Harry J., Purdue University, Lafayette.....M23
Reep, Geraldine, 3110 Broadway Ave., Indianapolis.....M30
Reeves, June, Converse M27
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Reynolds, Albert E., Staunton.....M29
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Reynolds, J. J., University of Notre Dame, Notre Dame.....M27
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Richter, Kenneth Murrel, 33 North Wallace Street, Indianapolis..M31
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Rippey, H. K., State House, Indianapolis.....M31
Ritchie, Earland, 1118 South Center, Terre Haute.....M31
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Roberts, Harry J., R. R. I, Lafayette.....M22
Roberts, Otis S., 328 South Grant, West Lafayette.....M25
Robertson, Frank S., Ewing, Box No. 7.....M24
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Rogers, Roy, North Madison.....M32
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Rosenbaum, John R., Wanatah.....M30
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Routien, John B., Montezuma.....M32
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Schafer, Pearl Catherine, Bremen.....M26
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Scofield, Robert, Crisman....M28
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Shaw, Otho, Griffin....M28
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Shontz, Geraldine, Indiana State Teachers College, Terre Haute....M31
Short, Darwin M., Owensville....M31
Showalter, Ralph W., c/o Eli Lilly Company, Indianapolis....M15
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Shuttleworth, Floyd Stephen, Alpine....M31
Silvey, Oscar W., College Station, Texas....M09
Simmons, V. M., Bluffton....M33
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Smiley, Elenore Rose, 143 West 35th St., Indianapolis....M31
Smith, Benjamin H., Indiana State Teachers College, Terre Haute..M25
Smith, Charles Piper, 976 Riverside Ave., San Jose, California....M03
Smith, Elmer A., 735 Ninth St., Secaucus, New Jersey....M26
*Smith, Ernest R., 628 E. Walnut St., Greencastle....M21, F33
Smith, Herbert F., 301 S. 8th Street, West Terre Haute....M29
Smith, Miriam Irene, 459 North Grant, West Lafayette....M29
Smith, Norman M., R. R. No. 1, Dillsboro....M28

Smith, Orrin Harold, 430 Anderson St., Greencastle.....M25
Smith, Pressnall, 2007 Gulford, Huntington.....M27
Smithberger, Andrew, 1516 Hildreth St., South Bend.....M27
Smoots, Lewis, 1307 Maple Ave., Terre Haute.....M29
Snow, Charles C., William St. and Fruit Ave., Oakland City.....M27
Sousley, Clarence P., Dept. Math., Rose Polytechnic Inst., Terre Haute.....M25
Southgate, Helen A., 1101 Washington St., Michigan City.....M14
Sowa, Frank J., Box 147, Notre Dame.....M30
Spahr, Raymond John, 200 Swede Street, Norristown, Pennsylvania.....M32
Spangler, Iva, Decatur (I).....M23
Sperry, Theodore M., 501 W. 31st Street, Indianapolis.....M28
Spindler, George W., 9 37th Street, West Lafayette.....M24
*Spitzer, George, 1000 Stadium Ave., West Lafayette.....M09, F33
Sprague, J. Maurice, Trafalgar.....M30
†Springer, Alfred, 312 East 2nd Street, Cincinnati, Ohio.....NR
Springer, H. Stewart, Box 62, Biloxi, Mississippi.....M24
Stair, Edward C., Purdue Univ. Dept. Horticulture, Lafayette.....M24
Stanley, Oran B., 917 East 46th Street, Indianapolis.....M29
Stanton, Joseph H., 624 Swan St., Terre Haute.....M26
Stark, Connie R., 245 South Arlington St., Indianapolis.....M25
Steele, Brandt F., 5703 East Washington St., No. 9, Indianapolis (I).....M24
Steen, Edwin B., 114 South 9th Street, Lafayette.....M33
Steers, Pearl Y., 432 North Riley Ave., Indianapolis.....M31
Steinbach, Leslie, 425 East Ormsby Ave., Louisville, Ky.....M29
Stevens, William S., 725 Shelby St., Indianapolis.....M33
Stewart, Raymond R., R. R. 17, Box 409A, Indianapolis.....M31
Stock, Orion L., Rose Polytechnic Institute, Terre Haute.....M25
*Stockdale, Paris, Ohio State Univ. Dept. Geol., Columbus, Ohio.....M18, F29
Stoelting, Dorothy, 318 North Arsenal Ave., Indianapolis.....M30
Stone, Ralph Bushnell, 615 Russell St., West Lafayette.....M14
Stout, Emmett Carl, 417 School Street, Crawfordsville.....M29
Stout, Wilber, 154 Erie Road, Columbus, Ohio.....M29
Stratton, Everett F., Cambridge City.....M27
Strickler, Alvin, Evansville College, Evansville.....M22
Strong, Martha Thompson, 923 Atwater Ave., Bloomington.....M33
Studebaker, Leo, Lucerne.....M28
Stults, Arline, R. R. No. 2, Box 232, Huntington.....M31
Stump, Lois R., R. R. No. 3, Bloomington.....M28
Sullivan, Russell, 1431 North Meridian Street, Indianapolis.....M30
Sullivan, Walter Thomas Jr., 113 South Hcopes Ave., Auburn, New York.....M30
Sulzer, Elmer G., University of Kentucky, Lexington, Kentucky....M18
Swain, Louise, 415 East State Street, Pendleton.....M27
Swanker, Wilson Abbs, 509 Lenox Road, Schenectady, New York..M29
Swanson, Caroline, 7816 Cregier Avenue, Chicago, Illinois.....M27
*Switzer, J. Elmer, 523 South Park Avenue, Bloomington.....M23, F26

Taggart, Matt F., 1528 Lincoln Way East, South Bend.....M27
Tallman, Arthur Wince, 616 West Allegan St., Lansing, Michigan..M28
Tarvin, Noble R., 222 Wiggins St., West Lafayette.....M32
Tasker, Roy Carleton, Zoological Laboratory, Cornell Univ., Ithaca, New York.....M22
Tate, James H. Jr., R. R. No. 4, Connersville.....M30
Taylor, George Osborn, 1832 South 58th Avenue, Cicero, Illinois..M22
Taylor, Merrel Arthur, 4143 Boulevard Place, Indianapolis.....M30
Teder, John H., Jasper.....M26
Terre, Wilbert Louis, 2730 Chicago Road, Chicago Heights, Illinois.M30
Terry, Oliver P., 215 Sheetz St., West Lafayette.....M14
Test, Frederick H., 511 Russell Street, West Lafayette.....M27
*Test, Louis A., 511 Russell Street, West Lafayette.....M18, F31
Teter, Eber A., 620 South Fess Ave., Bloomington.....M33
*Tetrault, Philip A., 124 Thornell Street, West Lafayette.....M14, F25
Tharp, William E., Bureau Chemistry and Soils, U. S. D. A., Wash., D. C. M25
Thom, Dorothy, 248 North Home Ave., Franklin.....M31
Thomas, Harry B., 610 North Lincoln St., Bloomington.....M33
Thompson, James T., Colorado Univ. Sch. Med., 4200 E. 9th Ave., Denver, Colorado (I).....M20
Thompson, Clem O., School of Education, Univ. Chicago, Chicago, Illinois M11
Thompson, Vesta, 521 Oakdale Drive, Fort Wayne.....M31
Thompson, Wallon Horace, R. R. No. 6, Madison.....M28
Thornbury, William David, Dept. Geology, Indiana Univ., Bloomington M24
Thorne, Mabel E., 311 South Cornell Circle, Fort Wayne.....M31
Thrasher, Mrs. John R., 4903 Washington Blvd., Indianapolis (I)..M21
Toole, Eben Henry, U. S. Dept. Agr., Bur. Plant Industry, Washington, D. C.....M17
Toussaint, Joseph A., 907 Lenox Ave., Utica, New York.....M32
Toussaint, Walter, 201 Second Avenue, South Charleston, West Virginia M28
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Tranter, Robert Reese, 448 East Madison St., Franklin.....M30
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Trent, Horace M., Dept. Physics, A. & M. College, Mississippi.....M28
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Trueblood, Audrey S., Bot. Dept., Univ. of Cincinnati, Cincinnati, Ohio M28
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Turner, B. B., Indiana Univ. School of Medicine, Indianapolis.....M16
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Tweedy, Ruth E., R. R. No. 5, Wabash.....M28

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Urey, George Monroe, R. C. A. Victor Co., Inc., 1500 Fifth Ave., Seattle, Washington M28
Valentine, Oscar Wendell, Knox.....M30
Vance, Ira W., Wallace.....M29
Vandivier, Leo E., Franklin.....M30
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Van Hoozen, Ethel J., R. R. No. 6, Fort Wayne.....M27
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Vogt, Richard R., R. R. No. 3, South Bend.....M30
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Von Osinski, William Philip, 1405 Jefferson, Laporte.....M32
Voorhees, Herbert S., 804 West Wildwood Ave., Fort Wayne.....M96
Voris, Ralph, Southwest Missouri St. Teachers College, Springfield, Missouri M24
*Wade, Frank B., Shortridge High School, Indianapolis.....M03, F14
Wallace, Frank N., State House, Indianapolis.....M20
Walerstein, I., Dept. Physics, Purdue Univ., Lafayette.....M33
Wallingsford, Duff N., 1603 West Adams St., Muncie.....M30
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Wedel, Arthur, Box 394, Sulphur Springs, Texas.....M24
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Wells, Milo, R. R. No. 4, Bloomington.....M33
Wemple, Margaret Louise, 109 Main Street, Ligonier.....M32
Wenninger, Rev. Francis J., Univ. of Notre Dame, Notre Dame..M20
Wenzke, Herman Henry, University of Notre Dame, Notre Dame..M27
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Wood, Morris W., Culver Military Academy, Culver....M32
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Zebrowski, George, Buck Creek....M20
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Zerfas, Leon G., Indianapolis City Hospital, Indianapolis....M21
Zetterberg, Clifford, New Point....M29

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Page
Abbott, R. B., paper 158
Acids, dissociation constants 142
Acoustical treatment 175
Alkaloids, progenitors of certain plant alkaloids 122
Amino acids, color reactions with phenols 132
Analysis of group III 118
Anatomy of two-bodied lamb 235
Anniversary publicity committee 9, 16
Archeological survey committee 8, 14
Auditing committee 8
Benzene, adsorptive capacity of, silicas for 99
Biological survey committee 8, 14
Birds of Tippecanoe County 228
Blanchard, W. M., paper 44
Botany and bacteriology section—
Chairman, T. G. Yuncker 13
Papers in Proceedings 48
Bradt, W. E., papers 72, 116
Briscoe, H. T., paper 142
Caldwell, W. I., paper 159
Cathode rays, demonstration of 192
Cellophane, coloring of 139
Chemistry section—
Chairman, Ned Guthrie 13
Papers in Proceedings 72
Color reactions of amino acids with phenols 132
Coloring cellophane 139
Committees for 1933-34 8
Conn, K. E., paper 99
Contributions to promotion of science 44
Cook, R. V., papers 193, 194
Cortez, S. H., paper 161
Cupferron, use in separation of iron from indium 125
Cuscuta, insect galls on 70
Davis, J. J., memorial for E. B. Williamson 23
Paper on insects 195
Deam, C. C., paper 48
Degering, E. F., papers 105, 127
Dielectrics, X-ray investigation of 182
Dolomitic limes, degree of hydration of magnesia 113
Dragonflies of Indiana 1932-33 211
Drosophila melagonaster, irradiation of 224
Editor's report 15
Electron diffraction 159
Elliott, S. E., paper 163
Ferguson, J. E., paper 169
Fletcher, W. A., paper 107

Page
Foundation report 14
Fox, E. L., paper 113
Friesner, R. C., Secretary for 1933 7
Fungi associated with ringworm, treatment of 56
Galls, insect galls on Cuscuta 70
Geodes, some unusual forms 155
Geology and geography section—
Chairman, E. R. Smith 13
Papers in Proceedings 154
Graam, D. G., paper 201
Grass, notes on Indiana species distribution 50
Grave, B. H., Chairman zoology section 13, 195
Green, Clarence, paper 116
Green, D. B., paper 171
Guthrie, Ned, Chairman chemistry section 13, 72
Hall effects in cast bismuth 185
Harmon, D. L., paper 175
Hartman, R. J., paper 99
Hiestand, W. A., paper 205
Hirudo medicinalis, the leech 205
Hufferd, R. W., paper 118
Indiana fauna—
Birds 228
Dragonflies 211
Insects—
Bees 200
Cereal and forage crops, insects of 195
Fruit trees, insects of 198
Shade trees and shrubs, insects of 199
Vegetables, insects of 197
Mammals 27
Shrimp, large fresh-water 218
Indiana flora—
New or rare plants (listed by C. C. Deam) 48
Grasses, new county records 50
Insect galls on Cuscuta 70
Insects of Indiana for 1933 195
Iron, separation from indium 125
Jamieson, W. A., paper 56
Jenkins, R. O., paper 158
Julian, P. L., paper 122
Junior Academy of Science—
Chapter list 262
Committee 9
Program 17
Kelch, R. V., paper 171
Knipp, C. T., physics teaching notes 192
Lamb, anatomy of a two-bodied lamb 235

Lark-Horovitz, K.— Page
Chairman, physics section....13, 158
Paper 182
Leech, respiratory metabolism of.... 205
Liquid oxygen, demonstration of production of.... 192
Logan, W. N., memorial for Gerard Fowke.... 20
Lyon, M. W., Jr., presidential address.... 27
Lyons, R. E., papers....107, 132
Macrobrachium Ohionis 218
Mammals of Indiana, their origins.... 27
Markie, M. S., Vice-president for 1933.... 7
Mastodon, The Garrett.... 154
Mathers, F. C., papers....113, 125
McCleary, R. F., paper.... 127
McCormick, R. N., paper.... 218
Membership committee 8, 15
List 238
Memorials for—
Danglade, Ernest 19
Fowke, Gerard 20
Williamson, E. B.... 23
Mercury spectrum, character of certain terms.... 190
Merthiolate, use of.... 56
Miller, F. M., paper.... 132
Minutes—
Spring meeting 12
Winter program meeting.... 13
Executive committee 14
General session 16
Junior Academy of Science.... 17
Montgomery, B. E., paper.... 211
New or rare plants to Indiana.... 48
Nitro compounds as oxidizing agents.... 107
Node formation on a weighted cord.... 194
Officers for 1933.... 7
Ogden, A. N., paper.... 182
Oxidation, catalytic oxidation of carbohydrates.... 105
Oxidizing agents, nitro compounds.... 107
Oxidizing hydrolysis of ozonides.... 136
Ozonides, oxidizing hydrolysis of.... 136
Past officers 10
Petersen, L. H., paper.... 185
Phenylalanine, new test for.... 132
Physics section—
Chairman, K. Lark-Horovitz....13, 158
Papers in Proceedings.... 158
Physics teaching notes.... 192
Piezo-electric effect 161
Pigeon, reticulocyte formation in.... 201

Page
Plant alkaloids, progenitors of 122
Plants new or rare to Indiana 48
Potzger, J. E., paper 50
Powell, H. M., paper 56
Presidential address 27
Prichard, C. E., paper 125
Program committee for 1933-34 ..... 8, 15
Projectile deflection 193
Publication of Proceedings committee 8
Quartz crystal excited piezo-electrically 161
Radio field intensities about Athens, Ohio 171
Relation of Academy to State committee 8
Research committee 9, 15
Resonance in violins 158
Respiratory metabolism in leech 205
Reticulocyte formation and temperature 201
Riebsomer, J. L., paper 136
Selenium, organic compounds of 72
Preparation of hydrogen selenide 116
Shrimp, large fresh-water species 218
Silicas, adsorptive capacity of 99
Simpson, P. F., paper 154
Singer, J. I., paper 205
Smith, E. R., Chairman of geology and geography section 154
Sound, effect on space currents 163
Space currents, effect of sound on 163
State library committee 9, 15
Steen, E. B., paper 224
Surface potentials, methods of measuring 169
Tallman, R. C., paper 136
Temperature, effect on reticulocyte formation 201
Test, F. H., paper 228
Test, L. A., papers 139, 228
Torrey, T. W., paper 235
Treasurer's report 15
Tryptophane, new test for 132
Ultraviolet irradiation, effect upon fecundity of Drosophila 224
Von Osinski, W. P., paper 155
Walerstein, I., paper 190
Weatherwax, Paul, Treasurer for 1933 7
Welcher, F. J., paper 142
X-ray investigation of orientated dielectrics 182
Yuncker, T. G., Chairman botany section 13, 48
Paper 70
Zinc ethyl, preparation of 127
Zoolgy section, Chairman, B. H. Grave 13
Papers in Proceedings 195